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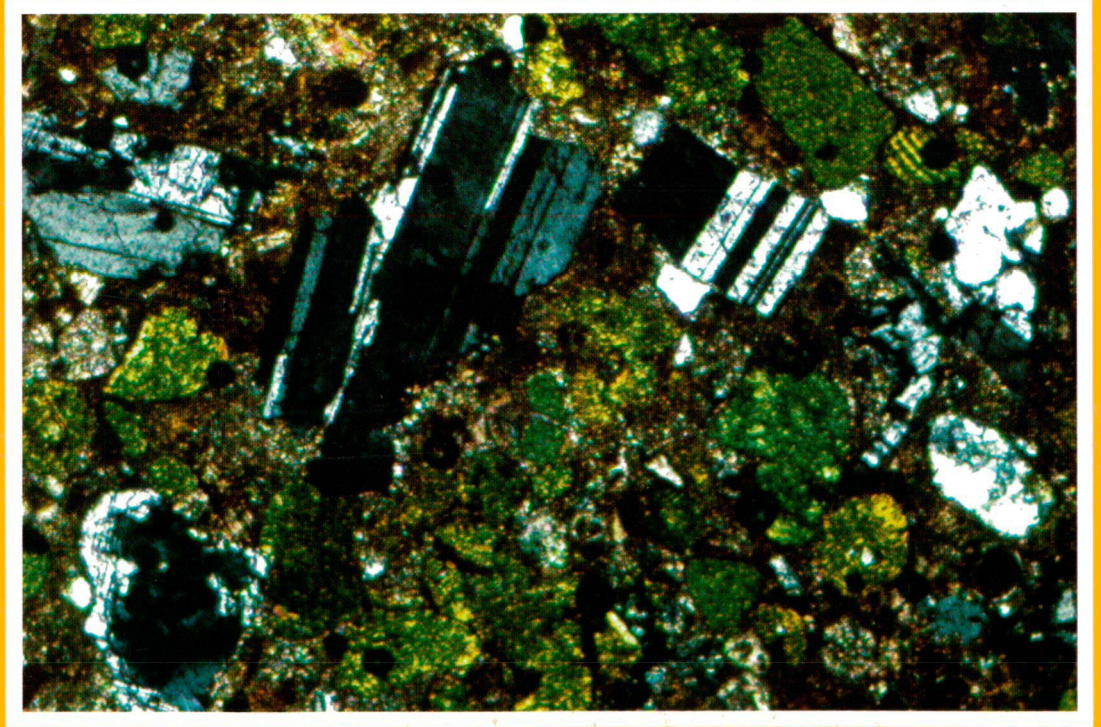
2ND MID-EUROPEAN CLAY CONFERENCE
Miskolc, Hungary, 20–24 September 2004



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On the cover:
Glauconitic grains surrounding unaltered feldspar crystals (thin section, crossed polarisers; field of view 2.5 mm). Upper Oligocene Eger Formation, Nyárjas summit, Novaj, Hungary. Photo: Judit Fekete.

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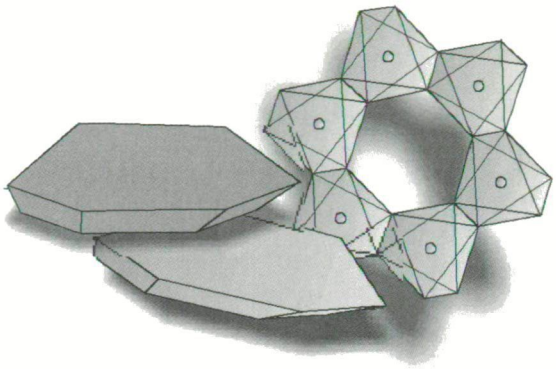

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Tibor Németh and Attila Terbócs

Abstracts revised by

János Földessy, János Kristóf, Imre Szabó, Géza Szendrei, Etelka Tombácz, István Viczián

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PREDICTION OF PETROLEUM GENERATION INTERVALS IN THE SOUTHERN NIGERIA RIFT BASINS BY MEANS OF CLAY TRANSFORMATIONS, VITRINITE REFLECTANCE AND FLUID INCLUSION STUDIES

AKANDE, S. O.,[1] VICZIÁN, I.,[2] ERDTMANN, B.[3]

[1] Department of Geology, University of Ilorin, Ilorin, PMB 1515, Nigeria
[2] Hungarian Geological Survey [Magyar Geológiai Szolgálat], Stefánia út 14., Budapest, 1143, Hungary
[3] Institut für Angewandte Geowissenschaften, Technische Universität, Str. des 17. Juni 135, Berlin, 10623, Germany
E-mail: sakande@skannet.com; samoakande@hotmail.com

Cretaceous to Tertiary rift basins in Southern Nigeria comprise of the Abakaliki and the Anambra basins, which form a part of the Lower Benue Trough. While hydrocarbon prospectivity in the Abakaliki basin was considered as high risk in view of the shallow thickness (cca. 2000 m) of the Pre-Santonian sediments, the adjacent Anambra basin with over 8000 m of both Pre-Santonian and Post-Santonian sediments have estimated reserves of 1 billion barrels of oil and 30 trillion cubic feet of gas.

A combined study of clay types especially smectite proportions in illite-smectite (S% in illite-smectite), mixed layers and illite "crystallinity" (IC) of clay constituents, vitrinite reflectance (Rom) on coaly particles and fluid inclusions microthermometry in the intraformational vein minerals from the Cretaceous to Tertiary sequences was carried out to evaluate the burial stages and thermal maturation of the sediments in selected oil exploratory wells and traverses across the two basins.

In the Abakaliki basin, where estimated palaeotemperatures vary from 170°C to 230°C; the clays are devoid of smectites S = 0%; illite "crystallinity" (IC) values are between 0.4 to 0.9°2Θ and vitrinite reflectance in oil (Rom) vary from 2.46 to 4.30%. In the adjacent Anambra basin where palaeotemperatures vary from 100 to 140°C, S% range from 20 to 30% and IC values are between 1.4 to 1.6 °2Θ, with maturity (Rom) values from 0.7 to 0.9%. If the zone of catagenesis, petroleum generation and expulsion is set at palaeotemperatures between 70°C and 130°C comparable with proportions of smectites in mixed layers (S% in I-S) between 40 to > 10% and maturity (Rom) values between 0.6 to 1.3%, our data suggests that source rocks in the Abakaliki basin have undergone burial diagenesis plus magmatic and hydrothermal effects leading to high palaeotemperatures. This level of overmaturity on the major axis of the Abakaliki basin indicate that the Albian to Cenomanian source rocks have higher chances of generating only gas. In the adjacent Anambra basin, the successions have undergone normal burial diagenesis (consequent to subsidence). The level of maturity attained suggests that the sediments are dominantly within the zone of petroleum generation and source rocks here comprising the Albian through Maastrichtian sequences have continued to generate hydrocarbons to date at stratigraphic intervals at least below the Cretaceous-Tertiary unconformity in the basin.

QUANTITATIVE RECONSTRUCTION OF HOLOCENE CLIMATE CHANGES BY MINERALOGICAL ANALYSIS OF PALAEOSOLS IN THE STEPPE REGIONS OF EAST EUROPE

ALEKSEEV, A. O.,[1] ALEKSEEVA, T. V.,[1] MAHER, B. A.[2]

[1] Institute of Physicochemical and Biological Problems of Soil Science RAS [Институт физико-химических и биологических проблем почвоведения РАН], Pushchino, 142290, Russia

[2] Centre for Environmental Magnetism and Palaeomagnetism, Department of Geography, Lancaster University, Bailrigg, Lancaster, LA1 4YW, United Kingdom

E-mail: alekseev@issp.serpukhov.su

The steppe soil belt of Eurasia, which includes the northern Caucasus, the low Volga basin, the southern Urals, and northern Kazakhstan, was investigated in this multidisciplinary study. Properties of palaeosols, as natural environmental recorders in the steppe belt, were compared with the sequence of environmental events. The work has shown that integrated mineralogical, magnetic methods can be used to obtain quantitative estimates of past climate, especially rainfall, changes, through both time and space.

About 6000 years ago, a new type of burial ceremony—erecting of a soil hill over a grave pit—appeared among steppe the tribes of the Eneolith epoch. Such archaeological monuments, known in Russian scientific literature as khourgans, are typical attributes of the southern Russian steppe landscape. Some burial complexes consist of several dozens or over hundreds of barrows, created within the Bronze Age (IV–II millennia B.C.), the Early Iron Age (I millennia B.C. – 4th century A.D.) and the early and developed stages of the Middle Ages (5th–14th centuries A.D.). Due to the well established chronological sequence of archaeological cultures it is possible to define the time of creation of the barrows quite precisely (from 200–300 to less then 50 years).

Understanding of palaeoclimate requires interdisciplinary work combining mineralogical, magnetic, pedological, microbiological and archaeological data. In this study, quantitative estimates of palaeoclimate changes through Holocene time were developed from analysis of the modern soil sequences, archaeologically buried soils. Soils can "record" information on solid phase mineral and retain this information in situ upon burial. Soil minerals are conservative part of soils, but furthermore they reflect the stage of soil development and the landscape-climatic situation at the moment of construction of the archaeological monument. Based on our previous work, we consider as most important the magnetic and mineralogical properties of the palaeosols, their humus content in the upper soil horizon, the depth of easily soluble salts, carbonates and their clay mineralogy.

Most recently, use of soil magnetite content as the basis of a quantitative climofunction (of rainfall) has been established for the area of the Russian steppe (Maher et al., 2002, 2003; Alekseev et al., 2003; Zavarzina et al.; 2003). Magnetic data, XRD, Mossbauer spectroscopy and analysis by electron microscopy show that the source of the enhanced magnetic susceptibility values in the Russian steppe soils is ultrafine-grained magnetite-maghemite. There is a strong statistical correlation between modern rainfall and the pedogenic magnetic susceptibility across the Russian steppe. This climofunction was then applied to the palaeosols of our study area to determine palaeorainfall. Hence, palaeorainfall can be calculated for each climate stage recorded in archaeologically buried soils.

The rate of formation of secondary ferrimagnetic minerals in soils is connected with the flux of Fe from primary Fe-bearing minerals. That is a function of the intensity and duration (time) of weathering. Once formed, Fe-oxides may be the subject to continual modification in an approach toward equilibrium with the changing soil environment. The investigation of sets of buried soils (a chronosequences spanning cca. 5000 years) from the steppe region does not confirm the fact that time is the main factor responsible for pedogenic enhancement of ferrimagnetic minerals concentration. Duration of the weathering determines the total pool of iron released from silicates and involved into formation of soil Fe-oxides in the connection with climatic conditions.

The obtained data allow to conclude that climate in the steppe soil belt of Eurasia over last 5000–6000 years had the cyclic character with alternation of humid and arid epochs of different degree and duration.

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EVOLUTION OF CLAY MINERALOGY OF PALAEOSOLONETZS DURING LATE HOLOCENE

ALEKSEEVA, T. V., ALEKSEEV, A. O., DEMKIN, V.

Institute of Physicochemical and Biological Problems of Soil Science RAS [Институт физико-химических и биологических проблем почвоведения РАН], Pushchino, 142290, Russia
E-mail: alekseeva@issp.serpukhov.su

Burial mounds (earth or stone hills) which are known in the Russian literature as "khourgans" appeared across large areas of the Eurasian steppes about 5000 years ago. Usually the khourgans have been considered as objects of studies for archaeology, ethnography, or other humanities and contain information about the culture of steppe inhabitants during the Bronze (III–II millennia B.C.), Early Iron (beginning I millennium B.C. – 4th century A.D.), and Middle Ages (5th–16th centuries A.D.). However, they also contain buried soils, which developed in ancient times and have been conserved in different degree of effectiveness by burial up to the present time. These buried soils reflect the state and changes of various components of the environment, in particular, climate, vegetation, and relief, in their profiles and thus can be used for the reconstruction of palaeoenvironmental conditions.

Two series of soils buried under khourgans from the desert-steppe area of Lower Volga were studied. The modern soil cover is characterised by complexity which is determined by surface microtopography. Soil complexes include chestnut soils and solonetzs. Solonetzs which occupy about 40% of the territory are confined to flat micro elevations whereas light chestnut soils and meadow chestnut soils—to slopes and depressions respectively. Soil series consisted from modern and buried light chestnut soils with different degree of salinity and solonetzs of the following ages: IV–III millennia B.C. (5000 years ago), 19th–17th centuries B.C. (3800 ya), 4th century A.D. (1600 ya) and 13th–14th centuries A.D. (600 ya) ("Abganerovo" set) and III–II millennia B.C. (4000 years ago), 15th–14th centuries B.C. (3500 ya), 2nd–3rd centuries A.D. (1700 ya) and 13th–14th centuries A.D. (600 ya) ("Malyaevka" set). The series of soils were examined by: soil chemical properties, clay mineralogy (X-ray diffraction and Mössbauer spectroscopy) and a range of magnetic measurements.

Recently a strong statistical correlation between modern rainfall and the pedogenic magnetic susceptibility across the Russian steppe has been obtained (Alekseev et al., 2003; Maher et al., 2003) and a quantitative climofunction (of rainfall) has been established. This climofunction was applied to studied palaeosols for quantitative reconstructions of rainfall variations for Late Holocene. The obtained data allow to conclude that climate on the territory under investigation over last 5000 years had the cyclic character with the alternation of humid and arid epochs of different degree and duration. The annual precipitation changed within 330–440 mm with the most arid 2nd–3rd centuries A.D. and the most humid 13th–14th centuries A.D. Solonetzs appeared on the territory under study 4000–5000 years ago and since that time they underwent considerable changes. Obtained data show that diagenetic transformations which take place in the profile of buried soils don't allow to use the diagnostic properties of solonetzs such as profile distribution of pH, humic substances and exchangeable cations for the reconstructions of palaeoenvironment It was shown that the most sensible and reliable indicators of solonetz process are the morphology of B horizon, textural differentiation of the profile and its clay mineralogy. The evolution of solonetzs resulted in the increasing of coefficient of contrast from 2 to 5 (this is expressed as a ratio of clay content in B horizon against A horizon). Clay illuviation was accompanied by the decreasing of smectite content in A horizon from 50–60% till 10%. Clay fraction from a top horizon of modern and buried solonetzs contains visible quantity of fine dispersed quartz. The mineralogy of B horizon is close to that of parent material. The presence of chlorite in the 30 cm upper layer of solonetzs buried before 14th century A.D. testifies the existence of rather mild weathering conditions. The climatic optimum of the Middle Ages (the period from the 12th to the 14th century) lead to the remarkable changes of solonetz properties such as double increasing of clay content and specific surface area of A horizon, destruction of smectites in B horizon, and destruction of chlorites in both A- and B horizons. Additional to morphological characteristics on the base of which this soil profile was attributed to residual solonetz is the high content of fine dispersed quartz in the clay fraction of A horizon. The restoration of solonetz characteristics including the textural and mineralogical differentiation took less that 600 years. Modern solonetzs are characterised by the decreasing of exchangeable Na and they in a comparison with buried soils can be regarded as Mg-solonetzs.

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BASIC CHARACTERISATION OF BENTONITE FROM LIESKOVEC, CENTRAL SLOVAKIA

ANDREJKOVIČOVÁ, S.,[1] HRACHOVÁ, J.,[1] MADEJOVÁ, J.,[1] KOMADEL, P.,[1] GALKO, I.[2]

[1] Institute of Inorganic Chemistry SAS [Ústav anorganickej chémie SAV], Dúbravská cesta 9, Bratislava, 84503, Slovakia
[2] Envigeo, Kynceľová 2, Banská Bystrica, 97411, Slovakia
E-mail: uachslav@savba.sk

The aim of this work is the characterisation of mineralogical and chemical composition of bentonite from the Lieskovec deposit. Thirty samples (L1–L30) were systematically selected from various parts of the deposit and analysed by X-ray powder diffraction analysis (XRD), infrared spectroscopy (IR), Mössbauer spectroscopy (MS), chemical and thermal analyses to identify the minerals present and to characterise the chemical composition of smectites. Cation exchange capacity (CEC) values provided information on the negative layer charge. The water vapour-sorption data at different relative humidities and the effect of soda ash treatment on sedimentation volumes were measured.

XRD patterns show that the dominant mineral present in all samples is a dioctahedral smectite. The impurities include: kaolinite and quartz in all samples and orthoclase, muscovite, pyrite and calcite in some samples.

OH stretching vibrations near 3620 cm^{-1}, complex Si-O stretching band centered at 1035 cm^{-1}, AlAlOH bending vibrations at 913 cm^{-1}, AlFeOH bending vibrations at 875 cm^{-1} and Al-O-Si deformation band at 531 cm^{-1} in the IR spectra indicate that a Fe-montmorillonite is the dominant mineral in this bentonite. Typical vibrations of kaolinite (the most intense band at 3690 cm^{-1}) and quartz (doublet at 800 and 780 cm^{-1}) confirm admixtures of these minerals in all the samples. Carbonates (band near 1440 cm^{-1}) were identified only in L22 and L24.

Preliminary results of MS show Fe(II) content below 5% of total Fe in bentonite and less than 10% of total Fe bound in Fe-oxohydroxides. This means that substantial amount of iron is bound in the layers of montmorillonite.

Sedimentation volumes for samples treated with soda ash are clearly higher than those obtained for untreated samples, however, they are lower than those obtained for soda activated Al-rich montmorillonite from Jelšový Potok (Slovakia).

These experimental results confirm that bentonite from the Lieskovec deposit is a clay containing Fe-montmorillonite (> 40%), other minerals present may include different amounts of kaolinite, quartz, orthoclase, muscovite, pyrite, carbonates and/or Fe-oxohydroxides, depending on the sampling location in the deposit. The montmorillonite contains substantially more iron in comparison with montmorillonites from other Slovak deposits. Soda activation improves rheological properties of the material.

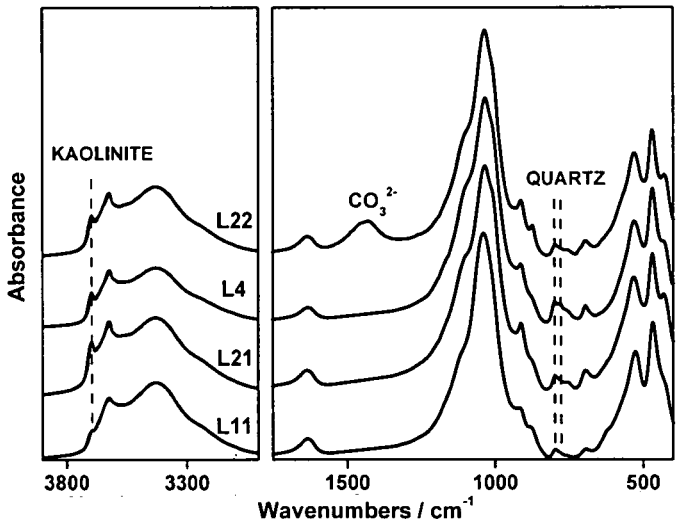

Fig. 1: IR spectra of less than 2 μm fractions of the samples L4, L11, L21 and L22

FACTORS AFFECTING THE REACTION PROGRESS OF PHYLLOSILICATES IN LOW-TEMPERATURE METAMORPHIC CONDITIONS

ÁRKAI, P.

Laboratory for Geochemical Research HAS [MTA Geokémiai Kutatólaboratórium], Budaörsi út 45., Budapest, 1112, Hungary
E-mail: arkai@geochem.hu

Certain phyllosilicate parameters such as the calibrated full width at half maximum (FWHM) values of the X-ray powder diffractometric (XRPD) basal reflections of illite-muscovite and chlorite have been widely and successfully used for determining diagenetic and metamorphic zones of rocks devoid of diagnostic or metamorphic facies-indicating minerals or mineral assemblages. These empirical parameters express the stage that was reached by a series of inequilibrium type structural and chemical transformations of clay minerals, i.e. the stage in inequilibrium processes called reaction progress.

Integrated XRPD, TEM, EMP, AEM, FTIR and other studies demonstrated that regular changes in proportion of swelling interstratifications (especially at lower grades), increase of mean crystallite thickness, change in shape of crystallite thickness distribution, and decrease of mean lattice strain (especially at higher grades) control these FWHM values formerly called "crystallinity" indices.

Temperature is generally regarded as the main, decisive factor that determines the reaction progress of phyllosilicates. In spite of this, "crystallinity" indices could never be used as geothermometers, and efforts aiming at the quantitative, overall valid correlations of these indices with other indicators of metamorphic grade (coal rank, mineral facies, etc.) failed because of

a) the inequilibrium nature of the reaction progress of phyllosilicates, and because

b) there are numerous additional factors that may influence considerably the processes mentioned above.

Some of these additional factors are: lithology, chemistries of bulk rocks and fluids, porosity and permeability of rocks, mineral chemistry, and various types of pressure (lithostatic, fluid, tectonic deviatoric) and strain, as well as the time derivatives of these factors (kinetic parameters).

At present, data and conclusions available in the literature on the effects of these factors are in part sporadic, and—to a great extent—controversial. This can be explained mostly by the fact that various, often extremely differing combinations of these factors may act in natural systems in function of geotectonic settings. Thus, additive or subtractive (extinctive) interrelations of these factors may result in strongly differing apparent diagenetic-metamorphic grades.

The lecture presents selected examples of case studies carried out with contributions of many colleagues from the Alpine and Carpatho-Pannonian regions in the past several years.

The effects of lithology and bulk rock chemistry on phyllosilicate assemblages, dioctahedral white mica and chlorite chemistries and "crystallinity" indices are discussed using characteristic formations from the Helvetic domain of the Swiss Central Alps, the Graz and Sausal Palaeozoic of the Upper Austroalpine Nappe System, Eastern Alps, the Palaeozoic of the Transdanubian Central Range and the Mesozoic of the Meliata unit (Western Carpathians).

Contrasting effects of tectonic shear strain on phyllosilicate characteristics in thin-skinned compressional settings are demonstrated by profiles cross-cutting the main nappe boundaries of the Helvetic domain, by profiles representing meso- (outcrop-) scale tight folds (Helvetic domain) and post-peak metamorphic mylonitisation in the Bükk Mountains (NE Hungary).

The effects of post-diagenetic fracturing on clay mineral behaviours are demonstrated on the example of a thick, monotonous albitic claystone formation from the Mecsek Mountains, Southern Hungary, which was selected for disposal of high-level radioactive wastes.

For complex interactions of the various factors could be proved in most of the investigated geological objects, only multi-methodological approach using petrographic (microstructural) observations, clay mineralogy, phyllosilicate "crystallinity" indices and organic maturity data may provide realistic results for petrogenetic interpretations.

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SMECTITES IN VESICLES OF THE ALKALI BASALTS FROM LOWER SILESIA, NW POLAND

AUGUST, C.

Institute of Geological Sciences, Wroclaw University [Instytut Nauk Geologycznyh, Uniwersytet Wrocławski], pl. M. Borna 9, Wrocław, 50 204, Poland
E-mail: august@ing.uni.wroc.pl

Alkali basaltic rocks from Lower Silesia (SW Poland) represent the eastern part of the Central European Cainozoic Volcanic Province. These volcanic rocks occur as lava flows, veins and necks, weathered and eroded for the most part. Nephelinites, basanites, tephrites and olivine basalts are most wide-spread.

Post-magmatic clay, zeolite and carbonate mineralisation is common and not preferably related to any of these rock types. The hydrothermal mineral associations crystallised in vesicles and other irregular cavities. Though generally no regular pattern is found in the spatial distribution of the mineralised zones, a stronger concentration of miaroles is observed near the top of lava covers, in particular the brecciated ones. Clay and zeolite mineralisation is very rare in the volcanic necks. There, the miaroles are mainly filled with calcite, aragonite and dolomite.

Clay minerals are represented only by smectites which occur in two generations in the miaroles: 1) trioctahedral saponite found on the surface of the miaroles and forming the base for zeolites, and 2) dioctahedral Mg-Fe-montmorillonite formed after the zeolites. The third smectite generation (a poorly crystalline dioctahedral Fe-smectite) is a beige to light pink mineral filling cavities and fissures in volcanic breccias.

The distribution and crystal chemistry of the post-magmatic mineral associations in the miaroles indicate that these minerals formed due to various post-magmatic hydrothermal processes. Saponite, Mg-Fe-montmorillonite and zeolites crystallised from solutions enriched in Mg, Fe, Ca, Na, and K originated from magma degassing during the final stage of lava cooling. The smectite found in volcanic breccias formed in a different process, probably linked with the decomposition of lepidomelane by low-temperature hydrothermal solutions rich in Si, Fe and Al, with minor Ca and K, partly of meteoric origin, penetrating the breccias.

The observed crystallisation sequence of the smectites and various zeolite species reflects changing temperature and composition of hydrothermal fluids in the miaroles. The smectites and zeolites stability diagrams show that Mg,Ca members of the mineral association crystallise at relatively high pH, high Si–Al and Na–K ratios, and high temperatures whereas at lower values of these parameters (but still relatively high Na–K ratio) crystallisation of Na zeolite is stimulated in hydrothermal solutions.

Table 1: Chemical composition of hydrothermal smectites in basaltoids from Lower Silesia, NW Poland

Component	Trioctahedral smectite				Dioctahedral smectite			
SiO_2	44.41	56.89	50.34	47.62	51.34	50.97	47.84	45.39
Al_2O_3	19.41	18.02	8.53	6.43	28.84	19.40	24.76	23.50
MgO	21.43	10.90	22.10	21.78	3.78	5.78	6.27	5.23
$Fe_{tot.}$	2.17	3.42	5.58	6.34	2.18	5.84	9.53	10.35
CaO	1.48	1.76	1.84	1.99	1.69	2.55	2.22	2.34
K_2O	0.07	0.66	0.15	0.23	0.43	0.65	0.69	0.48
Na_2O	0.03	0.01	0.12	0.12	0.49	0.59	0.93	0.99
TiO_2	–	–	0.09	0.02	0.02	0.02	0.13	0.20
MnO	0.22	0.02	0.06	0.02	0.02	0.05	0.17	0.14
Total	89.22	91.68	89.61	84.55	88.79	85.85	92.54	88.62

MAGNETIC IDENTIFICATION OF THE MAGNETIC MINERAL GREIGITE IN FINE-GRAINED SEDIMENTS OF LAKE PANNON

BABINSZKI, E.,[1] MÁRTON, E.,[2] MÁRTON, P.,[3] F. KISS, L.[4]

[1] Department of Geophysics, Eötvös Loránd University [Geofizikai Tanszék, Eötvös Loránd Tudományegyetem], Pázmány Péter sétány 1/c., Budapest, 1117, Hungary and
Geological Institute of Hungary [Magyar Állami Földtani Intézet], Stefánia út 14., Budapest, 1143, Hungary
[2] Eötvös Loránd Geophysical Institute, Palaeomagnetic Laboratory [Paleomágneses Laboratórium, Eötvös Loránd Geofizikai Intézet], Columbus u. 17–23., Budapest, 1145, Hungary
[3] Department of Geophysics, Eötvös Loránd University [Geofizikai Tanszék, Eötvös Loránd Tudományegyetem], Pázmány Péter sétány 1/c., Budapest, 1117, Hungary
[4] Research Institute for Solid State Physics and Optics HAS [MTA Szilárdtestfizikai és Optikai Kutatóintézet], POB 49, Budapest, 1525, Hungary
E-mail: babinszki.edit@geology.elte.hu

The Lake Pannon was a large, long-lived, brackish lake that occupied the Pannonian Basin during the Late Miocene. Magnetite was believed to be the typical magnetic mineral in the sediments of Lake Pannon, including its fine-grained beds. We observed, however, that the intensity of the magnetisation was very varied in the fine-grained sediments, which raised the question whether these sediments contain magnetite in different quantities or the difference is due to different magnetic minerals.

The first investigation indicated, that in some of the strongly magnetic sediments of Lake Pannon the carrier of the magnetic remanence was probably greigite. Since greigite is of diagenetic origin, i.e. definitely not coeval with the deposition of the sediment, its identification in a sediment is important from the viewpoint of palaeomagnetic or even more of magnetostratigraphic interpretation of the palaeomagnetic signal. Greigite can be identified by mineralogical methods. These methods need material separated from the sediment. However, separation is difficult, due to the small grain size, low quantity and the instability of the greigite. An alternative method is the magnetic. There is a series of magnetic mineralogical experiments which eventually lead to the identification of greigite. The methods are not destructive and although the process is time-consuming, the result is reliable, even if greigite is less than 0.01% of the mass.

With the magnetic method we were able to show that greigite is more common in the fine-grained sediments of Lake Pannon that magnetite. Surprisingly, the palaeomagnetic signal connected to greigite more often yielded statistically well defined mean direction than the one connected to magnetite. One possible explanation of this phenomenon is that magnetite, contrary to general opinion, can be of secondary origin in some sediments.

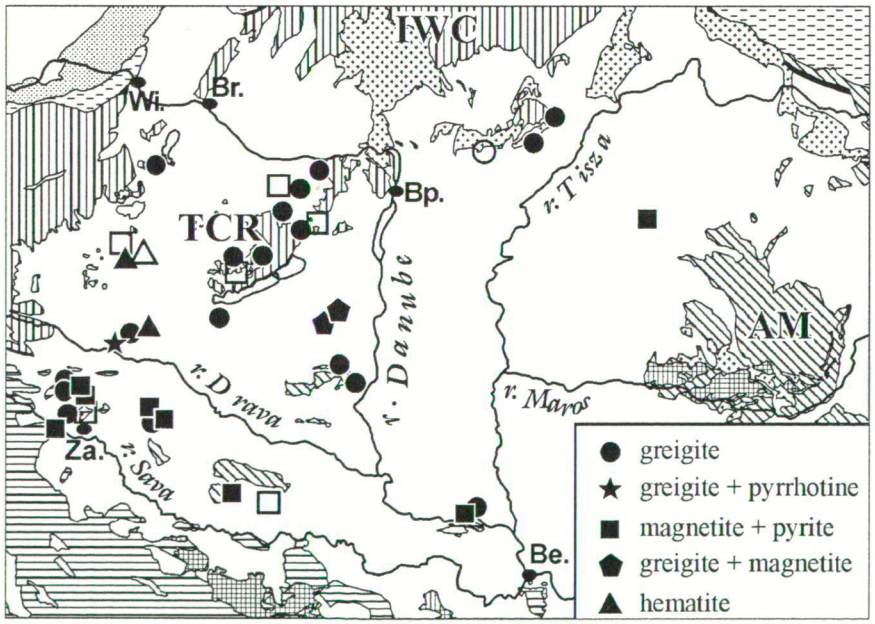

Fig. 1: Magnetic minerals occurrences in the Pannonian Basin. The full symbols show places where the palaeomagnetic signal is good, the hollow symbols show places where it is bad.

DYNAMIC SOIL CLAYS

BAIN, D. C.

Macaulay Institute, Craigiebuckler, Aberdeen, AB15 8QH, UK
E-mail: d.bain@macaulay.ac.uk

Soil clays, particularly expansible phases such as smectite and vermiculite, are very sensitive to the environment in which they occur and to any changes which occur to that environment. Because of the nature of the interlayer region, hydroxy-interlayered vermiculite and smectite are highly variable and changes in environmental conditions can be reflected in the degree of interlayer filling and in the relative stability of the interlayer components. The degree of interlayering in these phases is pH-dependent (Bain et al., 1990) and lowering of the soil pH by acid precipitation or change of land-use such as planting of trees on former arable land can result in the interlayer material being removed from hydroxy-interlayered phases. Modifications to hydroxy-interlayered clays are easily detected by conventional X-ray diffraction (XRD) techniques but more sophisticated XRD peak analyse routines are needed to detect more subtle changes in soil clay mineralogy. Application of such techniques to soils has shown that soil clays are dynamic systems which can change in quite short periods of time, as little as 30 years. Some examples of such changes will be presented.

Two weathering trends were established in a series of three brown forest soils in close proximity but under different land-uses in Scotland (Bain and Griffen, 2002): (1) an increasing proportion of vermiculite in interstratified mica-vermiculite in the upper horizons of the arable and forested soils; (2) formation of high charge corrensite by weathering of chlorite in all three profiles but least pronounced in the arable soil. The differences in clay mineralogy amongst the profiles are minor, but these two different weathering trends may be due to the effects of different land-use.

Research using methods to decompose XRD patterns of soil clay fractions from soils taken between 1913 and 1996 from agricultural experimental plots in the USA suggests that there is a significant influence of cropping method on the soil clays (Velde and Peck, 2002). Little change in clay mineralogy was seen in the rotation plot but there was a significant loss of illitic material from different phases for the plots with continuous corn cultivation. Use of NPK fertiliser since 1955 appears to have restored the clay mineralogy for the soils in continuous cropping compared to that for the 1913 samples.

Loss of K-bearing clay minerals such as discrete illite and interstratified mica layers and an increase in the formation of chlorite have been recorded in clayey red soils in flood irrigated Chinese rice paddies cultivated for 3, 10, 15, 30 and 80 years (Li et al., 2003). These changes occur over 30 years or less, a rather rapid, irreversible transformation of soil clay minerals.

In a chronosequence of poldered sediments in France, the natural mineral suite of kaolinite, mica, illite and two disordered illite-smectite phases have changed gradually but significantly over time under the influence of pasture development to a more smectitic clay assemblage (Velde et al., 2003).

These examples indicate that clay minerals in soils are dynamic systems that are affected by changes to their environment. Some changes to the clays are reversible but other changes can be irreversible.

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SORPTION OF CHROMATE BY CLINOPTILOLITE AND MONTMORILLONITE MODIFIED WITH ALKYLAMMONIUM SURFACTANTS

BAJDA, T., KŁAPYTA, Z.

Faculty of Geology, Geophysics and Environmental Protection, University of Science and Technology [Wydział Geologii, Geofizyki i Ochrony Środowiska, Akademia Górniczo-Hutnicza], al. Mickiewicza 30, Kraków, 30 059, Poland
E-mail: zklapyta@uci.agh.edu.pl

Clay minerals and zeolites modified with quaternary alkylammonium cations are frequently studied because of their potential application as environmental remediation materials. Some of these sorbents obtained using hexadecyltrimethylammonium bromide were shown to have the ability to remove Cr(VI) from aqueous solution. The aim of the presented work is to compare the chromate sorption capacity of selected minerals modified with hexadecyltrimethylammonium (C_{16}) and dioctadecyldimethylammonium ($2C_{18}$) surfactants.

In this study, clinoptilolite (Cl) from Dylągówka and montmorillonite (M) from Chmielnik (both localities in Poland) were used as starting materials. Their CECs determined by adsorption of alkylammonium ions are 16 and 95 meq/100g, respectively. The minerals were treated with C_{16} and $2C_{18}$ bromides in the amounts of 1.0 and 1.5 CEC. The products were characterised by IR spectroscopy, XRD as well as C and N determinations.

The sorption of chromate on the modified minerals was measured spectrophotometrically as a function of pH and concentration of Cr(VI) at the sorbent–solution ratio 20 g/dm^3. The amount of chromate removed from the solution gradually decreased with pH increasing in the range 1.3–10. At pH 2.6–3.1, the maximum sorption of Cr(VI) by the organo-zeolites (103–124 mmol/kg) was observed for the samples Cl–C_{16}–1.5 and Cl–$2C_{18}$–1.5 (Fig. 1) modified using 1.5 CEC concentration of C_{16} and $2C_{18}$ surfactants. Considerably lower values (37–46 mmol/kg) have been obtained in the case of the sorbents prepared at 1.0 CEC concentration of the alkylammonium ions (Cl–C_{16}–1.0 and Cl–$2C_{18}$–1.0). Similar relationship has been found for the organo-montmorillonites (samples M-C_{16}–1.0, M-C_{16}–1.5, M–$2C_{18}$–1.0 and M–$2C_{18}$–1.5) (Fig. 1), however, the maximum uptake of chromate (155–281 mmol/kg) was significantly higher in comparison with that observed for the organo-zeolites. At low concentrations of Cr(VI) (0–2 mmol/dm^3), its amount removed from the solution does not depend on the size of the alkylammonium ions bound to the mineral surface. In contrast, for more concentrated solutions the sorbents prepared using C_{16} surfactant show, as a rule, higher sorption capacity towards chromate than that obtained with $2C_{18}$ salt.

Acknowledgements

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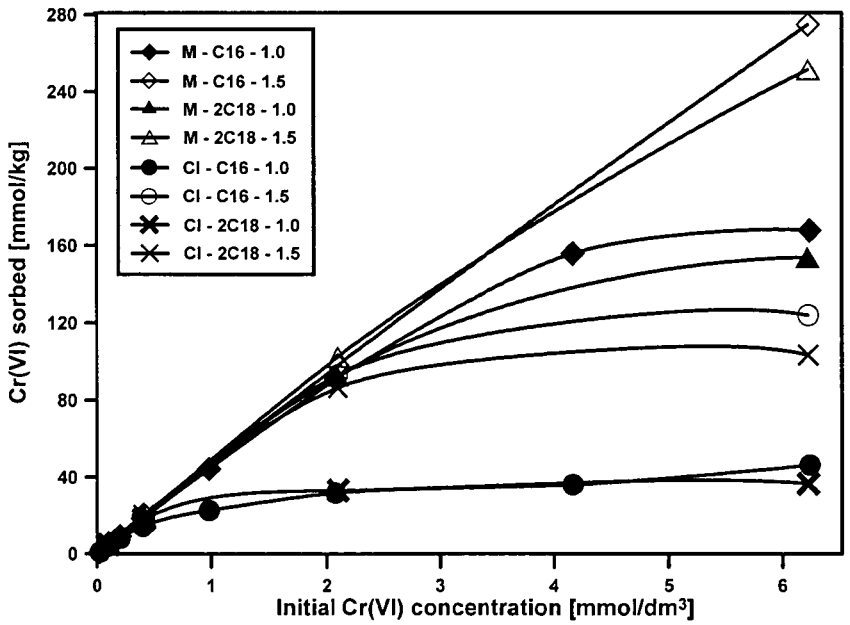

Fig. 1: Sorption of Cr(VI) by clinoptilolite (Cl) and montmorillonite (M) modified with C_{16} and $2C_{18}$ surfactants.

CLAY MINERALS WITHIN THE CARBONATE SEQUENCES IN TINJAN AREA (ISTRIA, CROATIA)

BARUDŽIJA, U., TADEJ, N., ALJINOVIĆ, D., VRKLJAN, M.

Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb [Rudarsko-geološko-naftni fakultet, Sveučilište u Zagrebu], Pierottijeva 6, Zagreb, 10000, Croatia
E-mail: ubarud@rgn.hr

Clayey limestones in the Upper Albian shallow-marine carbonate sequences from Tinjan area in Istria (Croatia) were investigated. Two layers of clayey limestone (70–90wt% of calcite) overlay the sequences containing carbonate breccias, interlaminated pelsparites-ostracodal micrites and cyanobacterial limestones as well as "quartz diagenetic sediments" (Barudžija, 2003). Insoluble residues of clayey limestones predominantly contain illite and/or mixed layer illite-smectite dominated by illite layers, illite-smectite with higher amount of smectite layers than previous and randomly interstratified minerals. Some of other phyllosilicates, probably smectites, are also present. Insoluble residues also contain quartz (10–20wt%), feldspars (up to 5wt%) and amorphous material. Since the appearance of the layers with clayey limestones in Upper Albian sequences in Istria is closely connected with the appearance of "quartz diagenetic sediments" (Durn et al., 2003), this mineral assemblage can be indicative of the origin of their parent material.

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CLAY PIGMENTS AS INDICATORS OF PAINT AUTHENTICITY AND MATERIAL PROVENANCE

BEZDICKA, P.,[1] GRYGAR, T.,[1] HRADIL, D.,[1] HRADILOVÁ, J.[2]

[1] Institute of Inorganic Chemistry AS CR [Ústav anorganické chemie AV ČR], Řež, 250 68, Czech Republic
[2] Academy of Fine Arts in Prague [Akademie výtvarných umění v Praze], U Akademie 4, Praha, 170 22, Czech Republic
E-mail: hradil@iic.cas.cz

Artist's pigments identified in colour layers of paintings are traditionally considered to be relevant for approximate dating based on literary evidence of exploitation, industrial production and use of different types of pigments in the history. Problems appear in older paintings, where written references are poor or missing and where, on the other hand, just the pigment presence is the only reliable evidence of its preparation and using in the fine art. This inconvenience together with difficulties caused by small size and heterogeneity of painting fragments, imprecise and frequently even incorrect interpretations of mineral assemblages in colour layers, caused that artistic styles are the only widely accepted headings of painting authenticity. Materials and technical features are underestimated—they are objective, but difficult to obtain and compare, especially because fragments with size less than 1 mm are available and only non-destructive techniques preserving sample stratigraphy are allowed to be used. Within this work we show the relation between chemical and mineralogical composition of clay pigments and their provenance. Additionally, the technology of pigment preparation from raw materials can be detected.

We have introduced powder X-ray microdiffraction as modern analytical tool suitable for the direct phase analysis of pigments from 0.1 mm spots on fragments of paintings. The method extends possibilities of traditional tools, optical and electron microscopy (SEM-EDX). X-ray microdiffraction is performed with common X-ray tube and monocapillary producing a quasiparallel beam combined with a sensitive-fast solid-state detector that enable diffractogram acquisition in less than 1 day in spite of so small sample size.

Phase analysis is unique for identification of earthy pigments, very common but diagnostically underestimated artists' materials. Earthy pigments containing clay minerals are of different colours: white, yellow, brown, red, green. We have found that mineral green earths found in paintings as distinct green or bluish green grains, simply called "celadonites", can have variable crystallochemical and phase composition. In some Bohemian wall paintings (Prague, Plasy) these grains are in fact chlorites. In Baroque paintings of A. Kern, celadonites with unusual crystallochemical composition could indicate that the author preferred one, probably unique material from a definite regional source. In earthy green-yellow layers, Fe-smectites are probably more common than it has commonly been expected; we identified green smectites as the main component of traditional Bohemian green earth from Kadan and in currently commercially available "Veronese" green earth.

Fatty red clay applied in Gothic paintings as adhesive ground for gilding ("poliment") was originally called "bole". The term was then extended to all red or yellow earthy grounds of various composition and origin. In fact, not all thin red grounds for gilding contain clays. In fragments of polychrome wooden funeral insignias of Czech kings from tombs in the Prague Castle, pure hematite red was used to give warm colour and the adhesive component should therefore be a protein binder, not clay. In Baroque bole grounds of paintings, direct phase analysis distinguished among materials of typical lateritic composition (kaolinite, hematite, anatase) and other low valuable boles with smectites and illites or, eventually, poorly crystalline goethite and jarosite. Additionally, further signs, revealed by combination of microanalytical methods, indicate that artists calcined or mixed materials of different origin. Because clay minerals are very sensitive indicators of natural processes, they bear unique signs of their regional orgin, and therefore they are extremely valuable for materials research of art works.

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X-RAY POWDER DIFFRACTION ON HEATED SUPPORT: NEW METHOD IN CLAY DIAGNOSTICS

BEZDICKA, P., GRYGAR, T., HRADIL, D., HRUŠKOVÁ, M.

Institute of Inorganic Chemistry AS CR [Ústav anorganické chemie AV ČR], Řež, 250 68, Czech Republic
E-mail: hradil@iic.cas.cz

Thermal behaviour of clays mirrors phase composition and structure. In multicomponent clay mineral mixtures, their dehydration and further transformation could be used as one of the fundamental diagnostic features reflecting structure and mineralogy. The interlayer space in expandable structures sensitively reflects temperature and humidity variations. The influence of the temperature on sorption and ion exchange processes on clays is discussed, for example, when evaluating clay barriers in the radioactive waste disposal. Dynamic behaviour of the interlayer space is not possible to monitor by conventional powder diffraction measurements of preheated samples, also because of full or partial reversibility of the process up to 300°C.

The powder diffraction measurements were performed in high-temperature XRD cell (Anton Paar HTK 16) with thin layers of samples deposited as methanol or water suspension of wet samples with diffractometer PANalytical X'Pert PRO, CoKα (30 kV, 45 mA) and X'Celerator detector. For identification of dehydration of clay minerals we performed thermal scan with step of 5°C starting from ambient temperature up to 300°C. At each step we measured one diffractogram in the angular range from 4 to 40° 2θ and examined the development of positions and integral intensities of basal reflections of expandable structures during the sample heating.

We have measured reference clay minerals, natural bentonites and sedimentary clays. In the example of smectite from Brodce dehydration of interlayer space occupied by different cations is compared. In all cases a continual reduction of the interlayer results in movement of the 001 diffraction towards d ≈ 10 Å. Differences are in the final temperature and mechanism of dehydration. Ca-Mg smectite contains water in two molecular layers and therefore intermediate single-layer structure is clearly visible at d ≈ 12 Å. When comparing monovalent cations, Na-interlayers dehydrate much easier than Li-interlayers; it could be explained by higher density of surface charge of Li^+.

Acknowledgements

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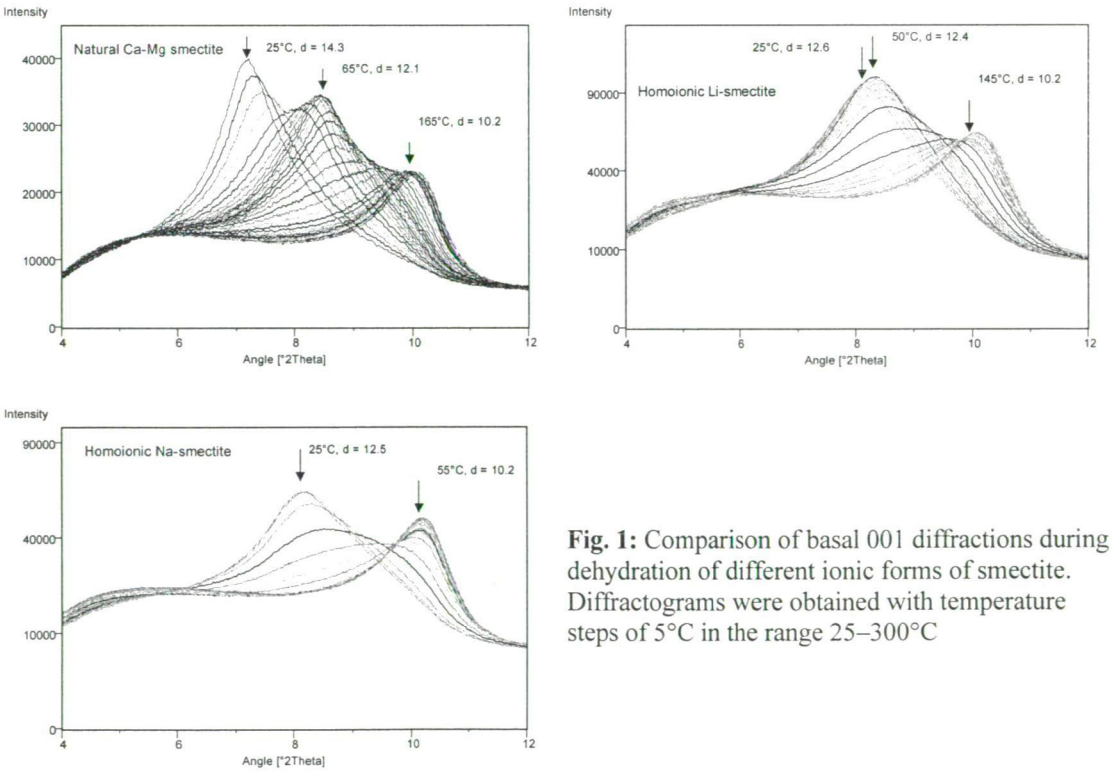

Fig. 1: Comparison of basal 001 diffractions during dehydration of different ionic forms of smectite. Diffractograms were obtained with temperature steps of 5°C in the range 25–300°C

CLAY MINERALOGY OF BENTONITES AND KAOLINS FROM KADAN AREA, CZECH REPUBLIC

BEZDICKA, P., GRYGAR, T., HRADIL, D., HRUŠKOVÁ, M., NOVOTNA, K.
Institute of Inorganic Chemistry AS CR [Ústav anorganické chemie AV ČR], Řež, 250 68, Czech Republic
E-mail: michaela.hruskova@iic.cas.cz

Tertiary sedimentary basin in the eastern foreland of Doupovske Mts. volcanic structure in NW Bohemia is rich in industrial clay deposits of economic importance. Kaolins, generally considered as products of intense chemical weathering of crystalline basement, are superimposed by volcano-sedimentary strata with argillised tuffs and bentonites closely connected with the beginning of volcanic activity in the Neogene. Argillisation of iron-rich tuffs with biotite and other mafic minerals led to formation of ferruginous smectites of yellowish or greenish colours. Beside their recent use as foundry bentonites, those of olive-green colour were also utilised as traditional mineral pigments. Their crystalline structure is difficult to describe—in older literature, foundry bentonites from the Rokle deposit are classified as "Ca-Mg montmorillonites of the Cheto type", green earth mined near Brodce and Úhošťany as "celadonite". Iron is a troublesome element even in some kaolins. When the kaolin which has been mined from the Merkur II deposit near Kadan has been left to dry in air, its colour locally changed to yellow and brown because of corrosion of small siderite nodules macroscopically invisible in primary material. A question of the origin of iron and carbon in siderite could also help to understand conditions of kaolinisation and post-kaolinisation and their eventual relation to the volcanic activity in the region.

We have used powder X-ray diffraction and microdiffraction, FTIR, diffuse reflectance spectroscopy in UV-VIS-NIR region (DRS) and voltametry to describe clay minerals with a particular focus on the forms of iron in samples from Rokle (bentonite and kaolin), Brodce (argillised tuffs and green earth), and Merkur II quarry (kaolin).

The clay fraction from Rokle and Brodce raw materials was separated by sedimentation in distilled water and the dominant content of smectites was proved by XRD. Homoionic clays were then prepared by ion exchange with NaCl and LiCl solutions, respectively. Migration of Li^+ ions into the structure (the Greene-Kelly test) was monitored by FTIR and re-expansion testing with ethylene glycol. As a result, smectites from both localities should not be classified as montmorillonites because of higher tetrahedral charge blocking the Li^+ migration and higher iron content in the octahedral sheet. Fe-smectite from Rokle is a final product of weathering sequence biotite-vermiculite-smectite. The parent material of green earth from Brodce was evidently different; beside biotite, titanomagnetite, and pseudomorphs after augite occurred in the fresh rock. The Fe-smectite contains more trivalent iron with structure closer to nontronite, divalent iron indicated by DRS, and magnesium. The step-scan of non-basal 060 diffractions region also clearly showed the presence of trioctahedral saponite-like structures. The presence of celadonite was not proved.

The origin of iron in some kaolins is different. In Rokle kaolin deposit, siderite nodules are missing, and only secondary hematite contamination occurs. In Merkur II quarry, siderite nodules contain Mg-rich siderite surrounding altered biotite fragments, which is the probable source of both iron and magnesium. The carbon in siderite is of a juvenile origin. Removal of divalent iron under reductive conditions of kaolinisation is therefore probably stopped in contact with hydrothermal CO_2-bearing waters. We have clearly documented the hydrothermal activity by the presence of unusual interstratified clay structures in studied kaolin samples. Original muscovite is transformed not only to illite and/or kaolinite by the process of normal chemical weathering, but also to expandable structures, only partly hydrated in their natural state. This is exfoliated mica rather than smectite. It is fully expandable with ethylene glycol and, interstratified with unaltered mica, gives a superstructural diffraction at $d = 27.0$ Å typical for R1 rectorite. Alteration is more intense in the bottom of the deposit, that also supports the hypothesis about the influence of tempered mineralised waters.

These results open the fundamental question of possible simultaneous course of volcanic activity in the region already during kaolinisation of crystalline bedrock elevations. Description of clay structures and mineralogical and structural forms of iron can be very useful in solving this question.

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MINERALOGICAL STUDY OF SOILS FROM WEST HUNGARY

BIDLÓ, A.,[1] BIDLÓ, G.,[2] GUCSIK, A.,[1] LÁSZLÓ, R.[1]

[1] Faculty of Forestry, University of West Hungary [Erdömérnöki Kar, Nyugat-magyarországi Egyetem], Bajcsy-Zsilinszky u. 4., Sopron, 9400, Hungary

[2] Department of Construction Materials and Engineering Geology, Technical University of Budapest [Építöanyagok és Mérnökgeológiai Tanszék, Budapesti Műszaki Egyetem], Műegyetem rakpart 3–9., Budapest, 1111, Hungary

E-mail: abidlo@emk.nyme.hu

The healthy growth of trees depends on the nutrient supply of the forest resources. There is no fertilisation in the different types of the Hungarian forests, because of the economical and natural conservation reasons. In this case, the nutrient supply of the forests is dominantly based on the content and cycling of nutrients in soils. The amount of the nutrients is strongly connected with the mineralogical contents of parent materials and rate of the weathering processes.

The purpose of this work is mineralogical and pedological studies of different types of soils from Iván and Sopron, West Hungary. After the descriptions and sampling of the soil profiles from the above mentioned sites, the chemical and physical characteristics of soils including pH-value (pH_{H_2O}, pH_{KCl}), acidity (γ_1, γ_2), $CaCO_3$-content, cation exchange capacity and exchangeable cations, particle size fractions, hygroscopic moisture content by Kuron, limit of plasticity by Arany, humus content, nitrogen content, AL-soluble K and P, as well as EDTA- and KCl-soluble nutrients. On the basis of standards, the mineralogical constituents were analysed by XRD using Náray-Szabó's and Péter Tiborné's methods and by derivatograph.

Soils at both sampling sites have been shown very acid and clayey loam physical characters. In general, the parent material (Iván: fluviosediments from River Rába; Sopron: weathered rocks from the metamorphic formations and fluviosediments of the Alps) is close to surface in the soil profiles.

Quartz plays an important role in the soil of site Iván, which corresponds to the strong weathering process in the regional geological settings. Moreover, in some cases, albite and microcline have been observed in specimens. Only one sample contains adularia, which probably was transported by seedlings. A little amount of muscovite was also presented in all of the samples. Anorthite was found in only two soil profiles. Illite, vermiculite, montmorillonite, chlorite and chamosite as sheet silicates were also identified in this area.

The soil profiles of Sopron mainly contain quartz, muscovite and albite. Anorthite and microcline (on the metamorphic based profiles) appeared in a few profiles. Sanidine was also found in only one sample. Clinochlor, leuchtenbergite, pennine and amesite as chlorites were also observed in variable amounts in all soil profiles.

Acknowledgements

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TG-MS ANALYSIS OF THE DESORPTION OF ORGANOCATIONS FROM SMECTITES.

BREEN, C., CHARLESWORTH, C., CLEGG, F.

Materials Research Institute, Sheffield Hallam University, Howard St., Sheffield, S1 1WB, UK
E-mail: C.breen@shu.ac.uk

The demonstrated improvements in mechanical and barrier properties together with the increased thermal stability of clay-based nanocomposites has attracted considerable attention.

Clay-based nanocomposites are attracting much attention because of the demonstrated improvement in mechanical and barrier properties, as well as thermal stability. The addition of only 5wt% organoclay in polypropylene raises the mechanical properties to those obtained when 30–60wt% of talc is added. This increase in property is accompanied by a decrease in component weight. An early drawback was a reduction in the time to ignition (TTI) in the nanocomposite compared with that for the virgin polymer which is now remedied by addition of low levels of conventional fire retardants. Even in the absence of conventional flame retardants the maximum in the heat release rate is significantly reduced. This marked improvement in the thermal stability of clay-based nanocomposites has resulted in a number of informative investigations into the thermal stability of the organoclay utilised in their production.

Uptake curves for the adsorption of a selection of organomodifiers, some with vinyl end groups, have been determined together with X-ray diffraction data and variable temperature DRIFTS spectra.

In particular we have used thermogravimetry-mass spectrometry (TG-MS) to identify the decomposition products arising from the thermal decomposition of the organoclays prepared at different loadings on cloisite-Na and other Na-saturated smectities.

In addition to linear alkanes and alkenes, a number of cyclic and/or aromatic compounds were produced by the organoclays. Moreover, the availability of the vinyl end groups is confirmed by the increased quantity of dienes, produced via the Hoffman elimination, present in the evolved gas stream.

TG-MS ANALYSIS OF THE DESORPTION OF ALKYLAMMONIUM IONS FROM SMECTITES WITH DIFFERENT IRON CONTENTS AND LAYER CHARGE

BREEN, C.,[1] FORSYTH, J.,[1] KOMADEL, P.,[2] JANEK, M.[3]

[1] Materials Research Institute, Sheffield Hallam University, Howard St., Sheffield, S1 1WB, UK
[2] Institute of Inorganic Chemistry SAS [Ústav anorganickej chémie SAV], Dúbravská cesta 9, Bratislava, 84503, Slovakia
[3] Helmholtz-Gemeinschaft Institut für Technische Chemie, Wasser- und Geotechnologie, Forschungszentrum Karlsruhe, POB 3640, Karlsruhe, 76021, Germany
E-mail: C.breen@shu.ac.uk

The demonstrated improvements in mechanical and barrier properties together with the increased thermal stability of clay-based nanocomposites has attracted considerable attention. For example, it has been shown that the addition of just 5wt% organoclay into polypropylene offers the same mechanical properties as the addition of 30–60wt% talc. Moreover, the overall thermal decomposition of the clay containing nanocomposite is enhanced. Unfortunately, the time to ignition (TTI) for the nanocomposite is often shorter than that of the virgin polymer but this can be remedied by the addition of conventional fire retardants at lower levels than those needed for the pristine polymer. This significant enhancement of the thermal stability of clay-based nanocomposites has led to a number of informative investigations into the thermal stability of the organoclay utilised in their production.

To date there has been no systematic study designed to correlate the relationship between the length of the alkyl chain on the surface modifying surfactant, the layer charge on the clay and the composition of the octahedral sheet. Here we use thermogravimetry-mass spectrometry to identify the decomposition products arising from octyl-, decyl-, dodecyl-, tetradecyl- and hexadecylammonium ions exchanged onto four smectites of varying charge and composition. We have used two source clays; SAz–1 (a high charge smectite) and SWa–1 (a ferruginous smectite) together with Jelšový Potok (medium charge montmorillonite) and Stebno (iron-rich beidellite).

In addition to linear alkanes and alkenes, a number of cyclic and aromatic compounds were produced by all the organoclays. The thermal decomposition of clay-organic complexes prepared using the shorter alkylammonium chains reached a maximum at lower temperature than those prepared using the longer chain species. The temperature and quantities of different desorbing species exhibited an element of correlation with the iron content in the clay structure.

NANOCOMPOSITE POLYMER ELECTROLYTES: EFFECT OF LAYER CHARGE ON THE INTERCALATION OF POLYETHYLENE OXIDE IN LAYERED SILICATES

BUJDÁK, J.,[1] HACKETT, E.,[2] GIANNELIS, E.[2]

[1] Institute of Inorganic Chemistry SAS [Ústav anorganickej chémie SAV], Dúbravská cesta 9, Bratislava, 84503, Slovakia
[2] Department of Material Science and Engineering, 214 Bard Hall, Cornell University, Ithaca (N.Y.), 14853, USA
E-mail: uachjuro@savba.sk

Polymer nanocomposites represent a radical alternative to conventional composite electrolytes. Of particular interest are Li salts dissolved in flexible polymers like polyethylene oxide (PEO). A serious drawback in these systems is the precipitous decrease in conductivity at temperatures below the melting temperature, which is typically above room temperature. One of the most promising ways to improve the electrochemical performance of polymer electrolytes is to form composite electrolytes by adding inorganic fillers.

Intercalation of PEO in layered hosts and in particular in layered silicates has been studied extensively. Based mostly on X-ray diffraction studies, there are two models: 1. The PEO adopts a helical structure inside the host galleries. The exchangeable cations reside inside the helix and are coordinated to the oxygen atoms of PEO. 2. The PEO chains are organised in an extended, all-trans bilayer parallel to the silicate surface.

The effect of layer charge on the intercalation of polyethylene oxide (PEO) was investigated using a series of reduced-charge montmorillonites and smectites with varying layer charge (fluorohectorite, saponite, three montmorillonite samples, nontronite and iron-rich beidellite).

Nanocomposites were prepared by solution or melt intercalation and using PEO of various molecular weights.

Melt or solution intercalation of PEO into layered silicates leads to essentially identical structure in the nanocomposite. The amount of intercalated polymer initially increases with layer charge but then decreases. In contrast the amount of water present after PEO adsorption continuously increases with layer charge. This is water mostly coordinated with the gallery cations. When PEO is intercalated it replaces water molecules filling the space between the hydrated exchangeable cations. No direct association between exchangeable cations and PEO oxygen atoms takes place. The amount of polymer adsorbed is controlled by the layer charge density, i.e. the surface area covered by the hydrated cations vs. surface covered by weakly adsorbed water. Molecular simulations confirm the experiments and show that the polymer oxygen atoms do not directly associate with the exchangeable cations, which are mostly coordinated to water molecules and surface oxygens atoms. The trends observed in this study may be applied to the intercalation-adsorption of layered silicates with other polymers or organic compounds.

INFLUENCE OF LAYER CHARGE AND CHARGE DISTRIBUTION OF SMECTITES ON THE RHEOLOGICAL AND SWELLING PROPERTIES OF BENTONITES

CHRISTIDIS, G. E.,[1] BLUM, A. E.,[2] EBERL, D. D.[2]

[1] Department of Mineral Resources Engineering, Technical University of Crete [Μηχανικών Ορυκτών Πόρων, Πολυτεχνειο Κρητησ], Chania, 73100, Greece

[2] US Geological Survey, 3215 Marine St., Boulder (Co.), 80303, USA

E-mail: christid@mred.tuc.gr

Layer charge of smectites is of economic and geologic importance, because it strongly affects significant smectite properties such as swelling, cation exchange capacity and ion exchange selectivity. Although the inhomogeneity of smectite layer charge is well documented, the significance of layer charge distribution on important physical properties of smectites has not been studied in detail. In this contribution we present preliminary data on the influence of layer charge distribution of 23 well characterised smectites, having variable layer charge and charge distribution, on important rheological and swelling properties of smectites. Determination of the layer charge and charge distribution of smectites was obtained using the LayerCharge program (Christidis and Eberl, 2003). The program compares XRD traces of K-saturated, ethylene glycol solvated smectites with computer simulated XRD traces calculated for three-component interlayering. Determination of rheological properties was carried out using a 35S Fann Viscometer according to API specifications (API 13A, 1993). Free swelling volumes were determined on Na-activated smectites according to Christidis and Scott (1996).

The rheological properties (apparent viscosity, plastic viscosity, gel strength) and the swelling capacity are proportional to the fraction of low charge (17 Å) layers (Fig. 1) and inversely proportional to the fraction of high charge (10 Å) layers in the smectites (not shown). Although, in general, smectites with low layer charge display superior physical properties, the total layer charge is not related systematically to any of the physical properties examined. Two quasilinear trends can be observed in the smectites studied (Fig. 1). One trend in each figure comprises high charge smectites with both tetrahedral and octahedral charge and the second trend contains low charge smectites and high charge smectites with predominately octahedral charge (Otay-type montmorillonites). Both trends are characterised by scatter. The observed scattering is attributed to the variable tetrahedral charge of the smectites. Indeed, it is observed that with increasing beidellitic component (i.e. increasing tetrahedral charge) both rheological and swelling properties shift to lower values and thus deteriorate (Fig. 1).

A similar dual quasilinear trend is observed when other rheological or/and swelling properties of smectites are correlated. These trends also show the influence of layer charge inhomogeneity on the rheological and swelling properties of smectites. It is suggested that rheological and swelling properties of smectites are controlled by the proportion of the low charge layers and the proportion of tetrahedral charge.

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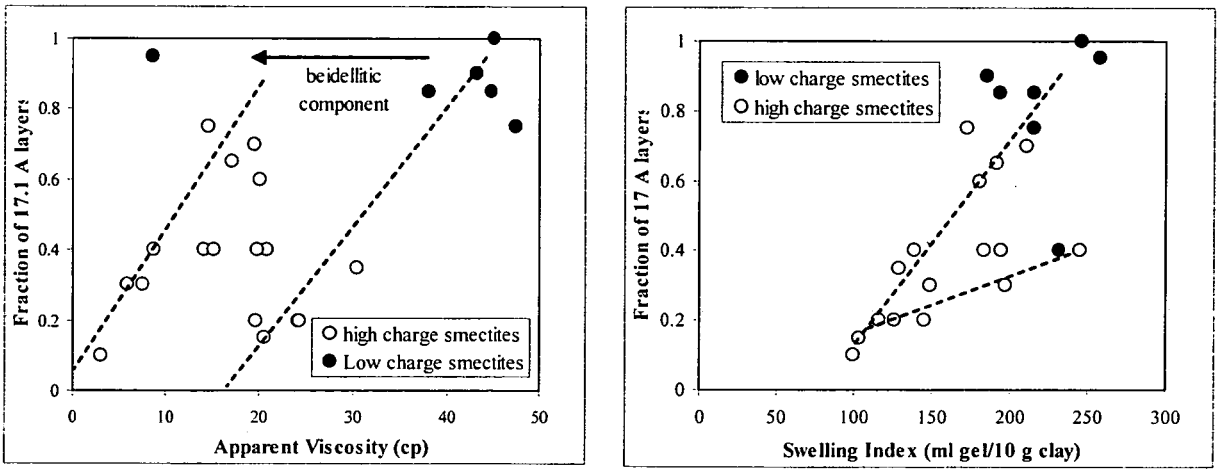

Fig. 1: Relationship between low charge layers and rheological and swelling properties of smectites.

BULK MINERALOGICAL CHARACTERISATION OF RESERVOIR ROCKS AND SANDSTONES USING DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY AND PARTIAL LEAST SQUARES ANALYSIS

CLEGG, F.,[1] BREEN, C.,[1] YARWOOD, J.,[1] HUGHES, T. L.[2]

[1] Materials Research Institute, Sheffield Hallam University, Howard St., Sheffield, S1 1WB, UK
[2] Schlumberger Cambridge Research, Madingley Road, Cambridge, CB3 0EL, UK
E-mail: f.clegg@shu.ac.uk

Within the oil industry, knowledge of the mineralogical composition of sandstone-based reservoir rocks is very important especially when complex multicomponent treatment fluids are applied to the reservoirs in order to enhance the oil extraction process (Borling et al., 1994). Other industrial areas interested in such analysis include: geophysics, construction, water industries and ceramics. Current bulk mineralogical analysis relies heavily on X-ray diffraction (XRD) and tends to be supported by infrared spectroscopy, chemical analysis and electron microscopy (Środoń, 2002). Combination of these techniques is time consuming and expensive yet still only 3–5wt% accurate.

Here, a Partial Least Squares Analysis (PLS) model created from Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) spectra of mineral mixtures has been formulated and is able to quantify each mineral component in an independent mineral mixture within 1.0wt% accuracy. An improved method for obtaining highly reproducible DRIFTS spectra was used, which was essential for accurate quantification within the PLS models. This methodology could also be applied to a variety of powdered samples including cements, soils, coals and minerals, which are also routinely analysed by DRIFTS (Kelvey and Britt, 1996). PLS is a multivariate statistical technique based on the PLS algorithm that can be used to quantify analyte components in infrared spectra, without the use of the Beer–Lambert Law (or its Kubelka–Munk equivalent for diffuse reflectance) (Beebe and Kowalski, 1987). This technique is especially appropriate when analysing complex multiple-component spectra, which contain many broad and overlapping bands. In essence the PLS algorithm examines regions of the spectra to determine which areas vary as a function of component concentration.

The seven mineral standards used in the PLS model of mineral mixtures were chosen to represent those typically encountered in sandstone-type rocks: quartz, dolomite, montmorillonite, illite, kaolinite, chlorite and albite. The results obtained from applying the PLS model of mineral standard mixtures to several sandstone-type quarry rocks and a suite of reservoir rocks from various depths of an oilfield were much better than anticipated given that the model did not describe the total variance of mineral components crystallinity expected in the rocks. The model was unable to differentiate between montmorillonite and illite due to their similar spectra, but was able to quantify their combined amounts. However, it was able to quantify the amount of albite in the quarry rocks in the presence of K-feldspar even though their spectra were very similar. A separate PLS model constructed using the DRIFTS spectra of the reservoir rocks showed that calcite and dolomite could be individually quantified despite their similar DRIFTS spectra. The model was also able to identify the type of clay present in the rock as montmorillonite and illite.

This feasibility study clearly demonstrated the high potential of a quick, accurate alternative method of quantifying bulk mineralogy in a sandstone-type rock by applying PLS analysis to their DRIFTS spectra. Moreover, the potential to improve quantification could be achieved by extending the model to include larger numbers of standards and real samples with data that covers all the expected variance in the rocks.

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THE ROLE OF THE TRANSVAPORISATION AND ALTERATION IN THE GENESIS OF NEOGENE INTRUSIVE HYALOCLASTITES OF HUNGARY

CSÁMER, Á.,[1] KOZÁK, M.,[1] KOVÁCS-PÁLFFY, P.,[2] DARÓCZI, L.[3]

[1] Department of Mineralogy and Geology, University of Debrecen [Ásvány- és Földtani Tanszék, Debreceni Egyetem], Egyetem tér 1., Debrecen, 4010, Hungary

[2] Geological Institute of Hungary [Magyar Állami Földtani Intézet], Stefánia út 14., Budapest, 1143, Hungary

[3] Department of Solid State Physics, University of Debrecen [Szilárdtestfizika Tanszék, Debreceni Egyetem], Egyetem tér 1., Debrecen, 4010, Hungary

E-mail: csamera@delfin.klte.hu

On the margin of a shallow fluid basalt and basaltic andesite intrusion an interaction between the magma and the wet, loose host sediment may occur which may cause quenching, chilling, or even a non-explosive fragmentation of the uplifting magma. The porosity of the loose sediment easily consumes the pressing energy of the moderately supplied magma columns and veins while arising bidirectional transvaporisation drives away a part of the products of the reactions. The glass-rich autoclasts emplaced as intrusives are autochtonous. Their appearance is not bedded, and exceptionally their transition to the less altered central facies (coarse blocked andesite, breccias, chambers, etc.) of the magma body is also exposed.

A basaltic tuff cone, called Lapos-Hegyestű (Tapolca Basalt Formation) is situated in the South Eastern part of the Kálla Basin (Transdanubia), near Kővágóörs village. In quarries on the slope of the Lapos-Hegyestű there are altered basaltic intrusions into the Upper Pannonian sedimentary basement (Kálla Gravel Formation) (Kozák et al., 1985). These altered intrusions of grey or yellow colour are steeply dipping, and contain halloysite formed by the alteration of the glassy basaltic rock. On the basis of thermoanalytical, X-ray and IR spectroscopic data it can be stated that these very rare, supergenic beds are generated by the effect of the humic acid bearing groundwater. However, the porphyric texture of the original basalt rock and the primary rock forming minerals can be recognised in thin sections.

In the Tardona Hills (North Hungary) there are exhumed small and shallow subvolcanic bodies on the margins of which altered aureoles and hyaloclastites containing andesite fragments occur (Kozák et al., 1998). According to the K-Ar dating of the samples collected from the investigated subvolcanic bodies, the age of the volcanic activity can be estimated to 9.5(±0.8)–13.73(±0.76) Ma BP. There are many places in the host Miocene sediment series (tuffite-sandstone deposits), where intruded andesite dykes can be found. Macroscopic features of these intrusions are similar to those of crystal tuffs, due to the formation of hyaloclastite. The syngenetic nontronitic-bentonitic alteration of the andesite dykes was generated by intensive groundwater migration. On the margins of these dykes limonitic bands can be found, too. Rarely, greenish epidote bearing zones may also occur indicating intensive interaction between the andesitic magma and the host sediment.

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KAOLINITE-SMECTITE: NATURE OF THE LAYERS AND MECHANISM OF SMECTITE KAOLINISATION

CUADROS, J.,[1] DUDEK, T.,[1] FIORE, S.[2]

[1] Department of Mineralogy, Natural History Museum, Cromwell Road, London, SW7 5BD, UK
[2] Instituto di Metodologie Avanzate di Analisi Ambientale, Tito Scalo, Potenza, 85050, Italy

The present study is aimed to contribute to a better understanding of the nature, formation and evolution mechanisms of mixed layer clay minerals by studying kaolinite-smectite (K-S).

We examined K-S from three different localities. Twenty specimens are from the Los Trancos clay deposit of Tortonnian age in Almeria, Spain (three samples are from palaeosols, the rest formed by hydrothermal activity). One sample is from a clay deposit formed by weathering of Eocene volcanic ash (Yucatan Peninsula, Mexico), and one from a Jurassic weathering crust developed on a bentonitic bed (Rushden, Northamptonshire, England). We used the < 2 μm particle size fraction containing K-S as a single phase.

The methods used in this study are the following: X-ray diffraction analysis of both random and oriented preparations, thermogravimetry (TG) and chemical analysis (X-ray fluorescence, wet analysis and ICP-AES). The proportion of kaolinite and smectite layers in K-S (%K) was calculated by fitting the experimental and theoretical XRD patterns calculated with the NEWMOD© computer program (Reynolds, 1985).

We find that the total dehydroxylation weight loss calculated from the TG curves is not linearly related to the evolution of K-S composition recorded by XRD. Thus, the collapse of layers to 7 Å is not linked directly to the increase of OH content of the octahedral sheet in K-S during the transformation. We interpret this trend as an effect of the development of patches within smectite layers in which part of the tetrahedral sheet is stripped off and OH groups are attached. The patches (henceforth called kaolinite-like patches) have the 1:1 layer structure, however they do not necessarily yield a 7 Å kaolinite spacing. At the beginning of the process, the patches are small and there is no change in the basal spacing. As the transformation proceeds, the point is reached when the patches become large enough to allow formation of 7 Å domains or layers, producing mixed layering. The TG curves of our samples show three dehydroxylation events: at cca. 450°C for kaolinite, cca. 620°C for smectite, and cca. 550°C for a component intermediate between them. We interpret the "intermediate" component as the parts of the smectite layers located in direct proximity of the kaolinite-like patches. Dehydroxylation of the octahedral sheet in these areas needs less energy than in smectite but more than in kaolinite, because the diffusion of the evolving H_2O is easier than in the former but more difficult than in the latter.

The chemical analyses show continuous release of Mg from K-S structure during smectite kaolinisation. In contrast, Fe remains in K-S or is removed much more slowly than the transformation happens. These data are supported by the non-linear evolution of the (060) peak position on the XRD patterns with increasing %K, indicating that the rate of change of the octahedral cation composition is lower than that of 7 Å layer formation. We associate this trend with the retention of Fe. The CEC examination indicates that some layer charge produced by the residual Al in the tetrahedral sheet is retained within kaolinite-like patches.

The evidence in this study indicates that the smectite-to-kaolinite reaction mechanism through mixed layer K-S is a solid-state transformation. We believe that the presented results apply to different environments of K-S formation. Our samples were formed in both hydrothermal and hypergenic conditions causing bentonite alteration. Also, K-S from palaeosols developed on chalk- and silica-rich rocks (Paris Basin, Brindley et al., 1983) and from present-day montmorillonitic soils (Alabama coastal plains, Karathanasis and Hajek, 1983) show the same relation between the dehydroxylation weight loss and K-S composition as in this study. Thus, smectite kaolinisation in non-bentonite systems proceeds also through the development of kaolinite-like patches, and our proposed mechanism operates in a variety of environments and conditions.

Our study also shows the complex nature of K-S layers. They can be partly smectitic and partly kaolinitic in terms of OH content, chemistry and basal spacing, and the smectite or kaolinite character of one layer can vary depending on the variable investigated.

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CHARACTERISATION OF THE LAYER CHARGE OF REDUCED-CHARGE MONTMORILLONITES

CZÍMEROVÁ, A., BUJDÁK, J.

Institute of Inorganic Chemistry SAS [Ústav anorganickej chémie SAV], Dúbravská cesta 9, Bratislava, 84503, Slovakia
E-mail: uachczim@savba.sk

A series of reduced-charge montmorillonites (RCMs) was prepared from SAz–1 montmorillonite (Arizona) saturated with Li^+ cations. Portions of the Li^+-saturated montmorillonite were heated at various temperatures (60–200°C) for 24 hours. The extents of the charge reduction were proportional to the preparation temperature. Series of RCMs provides a good model for studying the effects of the layer charge on properties of smectites. The layer charge of prepared samples was characterised by cation exchange capacities (CECs), layer charge density measurements using alkylammonium method and by means of spectra of organic, cationic dyes in clay dispersions.

The CEC values were measured and compared using several methods. These methods were based on ion exchange reactions with ammonium acetate, barium chloride, methylene blue (MB) and copper complex of triethylenetetramine. The values of CEC decreased with preparation temperature. There were non-significant differences between the CEC values determined by different methods. Only in the case of methylene blue adsorption, slightly higher values were observed due to MB adsorption above CEC.

The layer charge of the RCMs was measured using alkylammonium method. In comparison with the CEC values, this method gave information about the charge densities in the interlayer space of the minerals. Layer charge distribution histograms and average charge densities were calculated. The charge distributions of parent and all prepared RCMs are heterogeneous. The mean values of charge densities were used for the calculation of theoretical CECs.

The interactions of the prepared materials with two cationic dyes, methylene blue (MB) and thionine (Th) were studied in detail. Spectral properties of dye cations adsorbed at the silicate surface reflected significantly the charge density of the prepared materials. The distribution of the layer charge probably controlled the distances between adsorbed dye cations. The surfaces of high charge densities promoted and those of low charge densities suppressed the dye cation aggregation. The parent material with the highest charge density induced the formation of H-aggregates of the dye cations with sandwich-type molecular assemblies. The H-aggregates absorb light at significantly lower wavelengths with respect to monomers. The amount and the size of the H-aggregates decreased with decreasing layer charge in favour of H-dimers and monomers.

Comparisons of the spectral properties of adsorbed MB and thionine (Th) were investigated as well. The trends of the Th aggregation were similar to those of MB. Differences between MB and Th spectra were observed in the presence of high charge RCMs. Th exhibited a tendency to react on the surfaces of high charge silicates. This reaction is probably similar to those observed with other aromatic amines adsorbed on the clay mineral surfaces.

OPTIMAL SWELLING MODEL IDENTIFICATION UNDER THE INFLUENCE OF REACTIVE PHASE OF DRILLING MUDS

DEDE, M.,[1] BERDUFI, I.,[2] SHEHU, F.[3]

[1] Department of Physics, University of Tirana [Departamenti i Fizikës, Universiteti i Tiranës], bld. Zogu I, Tirana, Albania
[2] Institute of Nuclear Physics [Instituti i Fizikës Berthamore], POB 85, Tirana, Albania
[3] Trema Engineering Company, Tirana, Albania
E-mail: maridede@albnet.net

The swelling model of clay formations of well walls depends on the type of reactive fluid cations, including drilling muds, with which the wall clay interacts. For this reason, it is necessary to recognise the swelling type of a clay formation under the influence of various cations. The drilling technology should take into account the time it takes to achieve maximal swelling of a particular clay in a particular environment. This would ensure that action is taken within a limited time, before the swelling has reached its maximal values. In this way, the Tortonian clays have produced a lot of reservations during the drilling process of many deep and very deep wells in Albania. According to the identified models of swelling, it appears that they have a swelling of "zero" time, which means that as soon as they come to contact with the reactive environment they swell instantaneously.

Formations of swelling clays of these walls, even within a single well, behave differently in different depths towards active fluids which contain cations. This fact should be taken into consideration during the selection process of the chemical content of drilling muds used in a particular well.

The necessary time for maximal swelling of an ingredient of drilling mud (clay, polymer, filler etc.) is often relatively long. If a clay, polymer or another drilling fluid ingredient which has not yet reached maximal swelling is introduced to a porous layer of oil-gas, this will modify their tensioned conditions and consequently, supplementary tensions are created. If the ingredients have not completed the full swelling cycle, they will act as "blocking" agents during the continuing swelling process to the productive layer of oil, gas and retaining water.

The study argues the identification of the swelling model of clays under the influence of the active phase of reactive solution, which are exposed to the walls of the well.

The swelling model is identified based on the kinetic laws of swelling. The linear swelling model is based on the law $KdV/dT + V_0 = V_\omega$ (where V is the volume at the moment T, while V_0 and V_ω are at time $T = 0$ and ∞, respectively; K is a kinetic parameter, the time of swelling), and its linear form $B = CT$ (where $B=\ln[(V_\infty-V_0)/(V_\infty-V)]$ and $C = 1/K$).

The tests were carried out under the influence of different reactive solutions, which have simulated the filtration of drilling fluid used most often in the drilling technology. The correlation coefficients are evaluated and the most confident regression equations of the swelling models are made evident (Table 1). The swelling model is related to the specific structure of the clay. Structural specifications of clays are carried out with the techniques XRD, DTA, IR, CEC and TEM and are part of this study.

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Table 1:

Type of clay and reactive solution	Regression equation	Correlation coefficient
Clay of Divjaka well, exposed to distilled water	B=2.7705+0.010T	0.935
	B=2.824exp(0.00277T)	0.925
	B=0.101+0.83ln T	0.997
Clay of Divjaka well, exposed to solution 1% $CaSO_4$ ½ H_2O	B=0.335Texp(0.217)	0.943
	B=0.065+0.219lnT	0.862
	B=0.550exp(0.00093T)	0.981
Clay of Divjaka well, exposed to solution 1% $CaCl_2$	B=10.5251+0.288T	0.743
	B=4.731Texp(0.435)	0.998
	B=1.233+5.416lnT	0.884

STRUCTURAL, THERMAL AND SURFACE FORCE CHARACTERISATION OF MODIFIED LAYER SILICATES: RESULTS ON TALC, KAOLINITE AND MONTMORILLONITE

DELLISANTI, F., MINGUZZI, V., VALDRÈ, G.

Dipartimento di Scienze della Terra e Geologico-Ambientali, Università di Bologna, p.zza di Porta San Donato 1, Bologna, 40127, Italy
E-mail: franz@geomin.unibo.it

In the last decades nanostructured materials are receiving a great attention since their properties are different and often superior than conventional materials. In particular, many studies have involved the characterisation of silicate layered structures (e.g. clay minerals) which can be considered natural nanostructured materials since display size-dependent properties that make them useful as industrial raw materials and for many applications, such as environmental remediation. Lately, a great attention has been paid to study structural modifications of clay minerals after mechanical deformation via planetary ball milling, because it can induce nanostructuring and physical and chemical changes in the treated materials for new application techniques. Several studies concerning structural and textural changes by mechanical deformation of kaolinite (e.g. Horváth et al., 2003; Frost et al., 2001; Sanchez-Soto et al., 2000), talc (e.g. Pérez-Maqueda et al., 2004; Godet-Morand et al., 2002), and montmorillonite (e.g. Dellisanti and Valdrè, 2004; Christidis and Makri, 2003; Čičel and Kranz, 1981) were presented, however the available data are often incoherent. The aim of this paper is to show preliminary results from well characterised mechanical treatment of simultaneously compacted and shear stressed commercial Ca-montmorillonite, kaolinite and talc.

After mechanical grinding in controlled environment for 20 hours all analysed minerals have shown a severe broadening and decrease of intensity both in 00l basal diffraction peaks and in 060 peaks (XRD data). This indicates a reduction of crystallinity (increasing of FWHM values) and an increase of microstrain in treated sample respect to the untreated ones. Finally, only for the montmorillonite sample mechanical deformations have induced a progressive reduction of the d001 lattice spacing of the montmorillonite from 1.5 to 1.3 nm due to the expulsion of interlayer water molecules.

FTIR results have shown that the structural damage regards both the bonds in octahedral sites and between tetrahedral and octahedral sheets. A change is also observed in the ratio between OH-stretching band and hydrogen bond absorption band. Moreover, a slight broadening of the Si-O bond could also indicate an initial destabilisation of tetrahedral layers.

Thermal analysis (DTA, TG, DTG) has shown a reduction of weight loss relative to the expulsion of structural water during mechanical treatment. A decrease of the maximum temperature of dehydroxylation was observed for talc (ΔT = 100°C) and kaolinite (ΔT = 150°C) and in minor extent for montmorillonite (ΔT = 20°C).

Surface force analysis was performed by Atomic Force Microscope (AFM). Calibration curves were obtained using various layered silicates and preliminary results on talc and smectite showed different surface potentials.

The following results indicate that mechanical treatment via compression and shear involves structural destabilisation which could induce significant changes in chemical and physical properties of minerals. These modifications are very important for several industrial applications. Determination of particle size distribution, cation exchange capacity (CEC), specific surface and colour measurements (CIELAB system) are in progress.

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ADSORPTION AND ION EXCHANGE PROPERTIES OF ZEOLITE MATERIALS PRODUCED FROM FLY ASH USING SIMPLE METHODS OF SYNTHESIS

DERKOWSKI, A.,[1] FRANUS, W.[2]

[1] Institute of Geological Sciences PAS [Instytut Nauk Geologicznyh PAN], Senacka 1, Kraków, 31 002, Poland
[2] Department of Geotechnics, Lublin University of Technology [Katedra Geotechniki, Politechnika Lubelska], Nadbystrzycka 40, Lublin, 20 618, Poland
E-mail: ndderkow@cyf-kr.edu.pl

The production of zeolites by treatment of coal fly ash with alkaline solutions, was tested using various procedures of hydrothermal synthesis. The F class fly ash (classification: see Manz, 1999) is a good substrate for zeolite synthesis reaction because of its composition dominated by aluminosilicate and silicate phases. Based on previous work (Derkowski and Michalik, 2004), the most effective reactions of synthesis were chosen to produce three types of zeolite materials, rich in three zeolite phases: Na-X (FAU), NaP1 (GIS) and sodalite (SOD; nomenclature and classification after Baerlocher et al., 2001). The fly ash collected from Kraków power plant ($SiO_2 + Al_2O_3 = 72.5\%$; $SiO_2 / Al_2O_3 = 1.88$) was used as substrate for the reactions.

10 g of homogenised fly ash was mixed with NaOH and NaCl solutions, stored 24 hours in various temperatures (see below), under atmospheric pressure, then washed and dried. The reactions were carried out in the following conditions:

- the Na-X-rich material: 200 ml of 3 M NaOH, temperature 75°C;
- the NaP1-rich material: 200 ml of 1M NaOH + 100 ml of 3 M NaCl, temperature 150°C;
- the sodalite-rich material: 400 ml of 5M NaOH + 200 ml of 3 M NaCl, temperature 150°C.

The mineral and chemical composition of the raw fly ash and the products were determined using XRD, IR and EDS methods and SEM observations and their various properties were tested:

1. CEC (determined using Mn^{2+} ions, desorbed with 1 M CH_3COONa solution): fly ash 10 meq/100g; sodalite 63; Na-P1 154; Na-X 187.

2. Specific surface (SBET), specific surface and volume of mesopores (S_{mez}, V_{mez}) and micropores (V_{mic}) were measured applying adsorption and desorption of argon gas in liquid nitrogen temperature, and then calculation using Dubinin and Dubinin-Radushkievitsh equations (Brunauer et al., 1938; Ościk, 1979).

3. Thermal stability of zeolite materials was checked by heating in three ranges of temperature and then analysing their structures by XRD. Zeolite structures are stable: NaP1 < 300°C; Na-X ≈ 700°C, sodalite > 700°C.

Determined properties of zeolite materials suggest a broad range of possible applications. Na-P1 and Na-X materials show very high capacity for removing heavy metal ions from water solutions, due to their high CEC. Because of the wide micropore dimensions of 0.74 nm (Breck, 1974), significant micropore volume and the high thermal stability, Na-X may be an appropriate material for gas purification from SO_x, CO_x and Hg. NaP1 and sodalite have too small effective pore dimensions for accepting bigger gas molecules, but can be good adsorbents for water vapor.

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Table 1:

Material	S_{BET} [m^2/g]	V_{mic} [mm^3/g]	S_{mez} [m^2/g]	V_{mez} [mm^3/g]
fly ash	10	5	9	15
sodalite	28	11	18	29
NaP1	39	15	33	49
Na-X	231	90	46	71

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MINERALOGY OF CLAYS ON PERMO-TRIASSIC BOUNDARY TRANSITION IN KARAVANKE MOUNTAINS (BRSNINA SECTION)

DOBNIKAR, M.,[1] DOLENEC, M.,[1] OGORELEC, B.[2]

[1] Faculty of Natural Sciences and Engineering, University of Ljubljana [Naravoslovnotehniška fakulteta, Univerza v Ljubljani], Aškerčeva c. 12, Ljubljana, 1000, Slovenia

[2] Geological Survey of Slovenia [Geološki zavod Slovenije], Dimičeva 12, Ljubljana, 1000, Slovenia

E-mail: meta.dobnikar@ntfgeo.uni-lj.si

The end Permian mass extinction at approximately 250 Ma ago was one of the most severe mass extinction of the Earth. The high-resolution study of the two Permo-Triassic boundary sections in Western Slovenia (Idrijca Valley and Masore section) and one in the Karavanke Mountains (Brsnina section) reveal that the main extinction occurred over a period of less than 100,000 year. It is supposed to be coincidental with the terminal phase of the end Permian marine regression, the eruption of the Siberian basalts and with a sharp spike $\delta^{13}C$ carb, $\delta^{13}Corg$, $\delta^{18}O$ as well as by a negative Ce anomaly and the enrichment in several major, minor and trace elements at the P/Tr boundary which is represented in Idrijca Valley section in clayey marl layer (0.8 cm) and in Brsnina section by a boundary clay (1 cm). In this study we represent the XRD-analyses of clay and/or clayey marl layers from the Upper Permian to Lower Triassic sedimentary sequence of the Brsnina section in the Karavanke Mountains. The aim of this study was to reveal the possible changes in the clay minerals composition at the P/Tr boundary transition most probably due to increased erosion and environmental changes which are supposed to suggest a causal relation between Siberian volcanic activity and significant impact on land and land species as well.

TEM-STUDY OF MUSCOVITE-CHLORITE MIXED LAYERS IN A SLATE FROM THE PUNCOVISCANA FORMATION (SALTA PROVINCE, ARGENTINA)

DO CAMPO, M. D.,[1] NIETO, F.[2]

[1] Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Pabellón INGEIS, Buenos Aires, 1428, Argentina
[2] Departamento de Mineralogía y Petrología, Universidad de Granada, Avenuda Fuentenueva s/n, Granada, 18002, Spain
E-mail: nieto@ugr.es

Mica-chlorite mixed layers were identified by X-ray diffraction (XRD), as a major or a subordinate phase, in several slates of the Puncoviscana Formation from Sierra de Mojotoro (Easter Cordillera, NW Argentina). In order to determine the crystal chemical characteristics of these mixed layers and interpret its petrological meaning, the anchizonal slate P90 (Kübler Index = 0.30) was chosen for TEM observations as it displays less evidences of retrograde alteration of clay minerals than other slates of the area (Do Campo, 1999; Do Campo and Nieto, 2003). In this slate dioctahedral mica and chlorite form interleaved phyllosilicate grains up to 110 μm long, preferentially oriented with (001) sub parallel to slate cleavage, which forms an angle of 70° with bedding.

In agreement with XRD results the main phyllosilicates identified by TEM, were dioctahedral mica and 10–14 Å mixed layer, with chlorite in subordinate amounts and scarce smectite. The electron diffraction (SAED) patterns obtained for the 10–14 Å mixed layers present the following reflections in 001 row.

B134: 12.0 Å, 7.4 Å, 5.9 Å, 4.6 Å, 3.7 Å, 3.2 Å, 2.8 Å, 2.6 Å, 2.3 Å, 1.9 Å, 1.8 Å. (CV = 2.6%)

B137: 22.2 Å, 12.0 Å, 7.7 Å, 6.1 Å, 4.7 Å, 3.9 Å, 3.4 Å, 2.9 Å, 2.6 Å, 2.3 Å, 2.2 Å, 2.0 Å (CV = 2.6%).

B140: 12.2 Å, 7.8 Å, 6.2 Å, 4.8 Å, 3.5 Å, 3.0 Å, 2.7 Å, 2.4 Å, 2.0 Å, 1.7 Å (CV = 1.6%).

The coincidence between XRD and SAED data is quite good though the shape and position of the first peak in XRD traces (002 reflection) seems to be affected by the presence of smectite. In both cases reflections at 7.3–7.4 Å that could be attributed to chlorite appear. The coefficients of variation (CV) obtained for these patterns are clearly higher than the value of 0.75% established by AIPEA for rational XRD patterns (Bailey, 1982); therefore they represent random mixed layers. Besides, in $k \neq 3n$ rows the patterns present line and scarce points elongated along **c***, irregularly spaced. In lattice fringe images a sequence of irregular stacking to produce apparent 24 Å (10 + 14) layers could be observed, but frequently it is possible to distinguish the 10 Å layer from the adjacent 14 Å layer. In nearly all packets 14 Å layers prevail, exhibiting 14 Å/10 Å ratios between 1:1 and 3:1. The 10–14 Å pair appears repeated until seven times; this order is broken by stacking faults (10–14–14–10), or for excess 14 Å layers or less frequently 10 Å layers. Several open layers were identified in these packets.

Scarce diffraction patterns characteristic of chlorite, with semi-random or less frequently ordered stacking, were obtained. In lattice fringe images layers at 10 Å in ratios from 1:4 to 1:10, some of them open, interleaved among predominant 14 Å layers were observed in almost all packets. The 10–14 Å pair is not repeated more than three times consecutive and several lateral transformation from 14 Å to 10 Å layers was imaged.

The straight and continuous appearance of lattice fringes in all the mixed layer packets imaged plus the few open layers identified, let us conclude that they correspond principally to mica-chlorite mixed layers. However, scarce smectite layers could be present. The AEM analyses carried out for these packets clearly indicate that they correspond to interstratifications of chlorite-like and muscovite-like layers. The main cation in interlayer site is K, sometimes accompanied by Ca. In some cases the interlayer charge is lower than expected for muscovitic layers, which could be reflecting the existence of illitic substitution in 10 Å layers. Besides, several analyses exhibiting low (Fe + Mg)/Si contents may represent complex muscovite-chlorite-smectite mixed layers.

The structural site in which muscovite-chlorite mixed layers appear together with the observed along layer transformations from 14 Å to 10 Å let us interpret them as the result of a prograde metamorphic replacement of chlorite in porphyroblasts by dioctahedral mica layers, probably in presence of an aqueous fluid.

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SORPTION OF AS(V) ON TREATED AND UNTREATED CLAY MINERALS

DOUŠOVÁ, B.,[1] KOLOUŠEK, D.,[1] MARTAUS, A.,[1] FUITOVÁ, L.,[1] MACHOVIČ, V.,[2] GRYGAR, T.[3]

[1] Department of Solid State Chemistry, Institute of Chemical Technology [Ústav chemie pevných látek, Vysoká škola chemicko-technologická], Technická 5, Praha, 166 28, Czech Republic
[2] Institute of Chemical Technology AS CR [Vysoká škola chemicko-technologická AV ČR], Technická 5, Praha, 166 28, Czech Republic
[3] Institute of Inorganic Chemistry AS CR [Ústav anorganické chemie AV ČR], Řež, 250 68, Czech Republic
E-mail: Barbora.Dousova@vscht.cz

The adsorption of arsenic on clay surfaces is very important for the natural and simulated removal of arsenic species from aqueous environment. In this investigation four samples of clay minerals (natural kaolin and metakaolin from the same region, natural clinoptilolite-rich tuff and synthetic zeolite) in both untreated and treated forms were used for the sorption of arsenate from model aqueous solution. The treatment of minerals consisted of exposing them to concentrated solution of Fe(II). Within this process the mineral surface has been probably laden with Fe(III) (oxidohydr)oxides whose high affinity for the As(V) adsorption is well known. Two of the used mineral samples (natural clinoptilolite-rich tuff and synthetic zeolite) were also activated by HCl solution. This treatment suggested the increase of Si–Al ratio due to the dealumination and the removal of carbonates in the water washing stage after HCl treatment.

In all investigated systems the efficiency of As(V) sorption increased significantly with the use of the Fe(II) treated sorbents (from about 15% to more than 90%, Fig. 1), while the acid activation slightly improved only the sorption capacity of synthetic zeolite (to about 60%, Fig. 2).

The mechanism of treating process via Fe(III) laden surface was confirmed by voltametric analysis and diffuse reflectance spectroscopy. The investigation of untreated and treated sorbents indicated the presence of free Fe^{3+} ions or ferrihydrite in the treated samples. IR spectra of treated solids corresponded well to the above mentioned results showing significant bands caused by Fe(III)-SO_4, Fe(III)-O and As-O vibrations. In untreated solids no significant As-O vibrations were observed due to the negligible content of sorbed arsenate.

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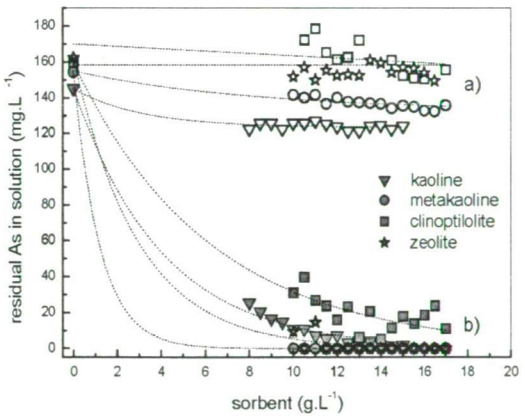

Fig. 1: As sorption with the use of the Fe(II) treatment; a) untreated sorbents (empty symbols), b) treated sorbents (full symbols)

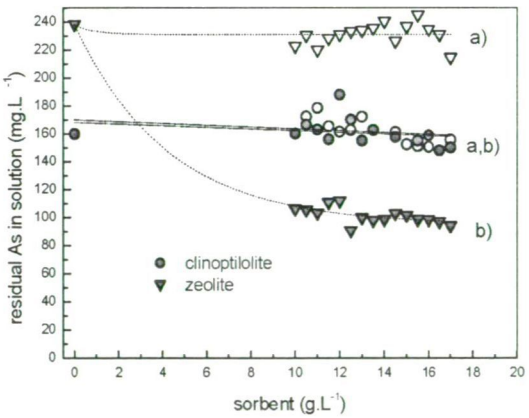

Fig. 2: As sorption with the use of the HCl activation; a) untreated sorbents (empty symbols), b) treated sorbents (full symbols)

MODIFICATION OF THERMAL BEHAVIOUR OF KAOLIN CLAYS BY ULTRASONIC TREATMENT

DRAPAŁA, J.,[1] WIEWIÓRA, A.,[1] PÉREZ-RODRÍGUEZ, J. L.[2]

[1] Institute of Geological Sciences PAS [Instytut Nauk Geologycznyh PAN], Twarda 51–55, Warszawa, 00 818, Poland
[2] Instituto de Ciencia de Materiales de Sevilla, Universidad de Sevilla, Isla de la Cartuja, Sevilla, 41092, Spain
E-mail: jdrapala@twarda.pan.pl

The present study examines the effect of sonication on the thermal behaviour of kaolinite. Selected well ordered sedimentary kaolin clays from Lower Silesia (Poland) (Maria and Zofia) were chosen to describe this effect. Ultrasonic treatment of raw samples was performed in cycles of 1, 3, 9, 21 and 40 hours. Sonication process caused change of surface area value from 15 m^2/g (for raw samples) to 39 m^2/g (for 40 hours) for Maria and from 15 m^2/g to 34 m^2/g for Zofia. After final stage of applied processing no more size reduction was observed. The (001) reflections of all treated samples of kaolinite were used to obtain best mean particle diameters calculated by MudMaster program (Eberl et al., 2000). Thickness of domains of coherent scattering for both kaolinites changes suitably from 0.049 μm for raw sample till 0.045 μm for Maria and from 0.049 μm till 0.040 μm for Zofia after 40 hours of ultrasonic treatment. When sonication time increases, the original dehydroxylation effect shifts to lower temperatures (Fig. 1) and decreases in intensity. At the same time the exothermic effect, previous to the mullite formation, shifts to lower temperatures and broadens. Comparison of the HTXRD patterns (Fig. 2) of the untreated and the sonicated sample during 40h shows that (001) reflection of the treated sample decreases considerably stronger than the (001) reflection of untreated kaolinite. It disappears at 600°C indicating end of the dehydroxylation process. The conducted investigation of the surface area, the DTA-TG curves and the HTXRD patterns showed that the structure and the thermal behaviour of kaolinites were strongly affected by the ultrasound treatment.

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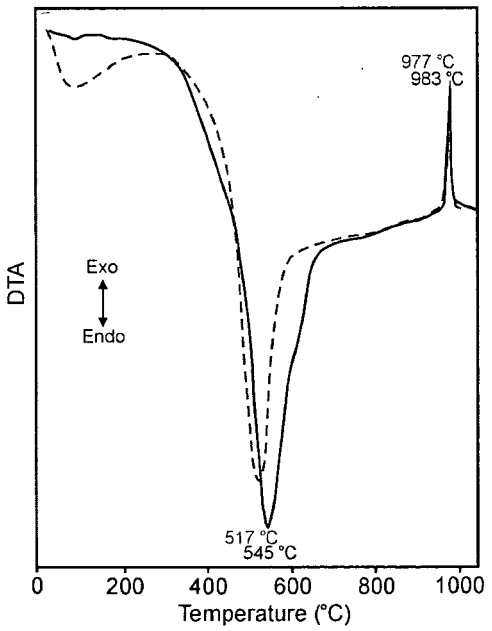

Fig. 1: DTA curves of the untreated Maria kaolinite (solid line), 40 hours sonicated (dashed line)

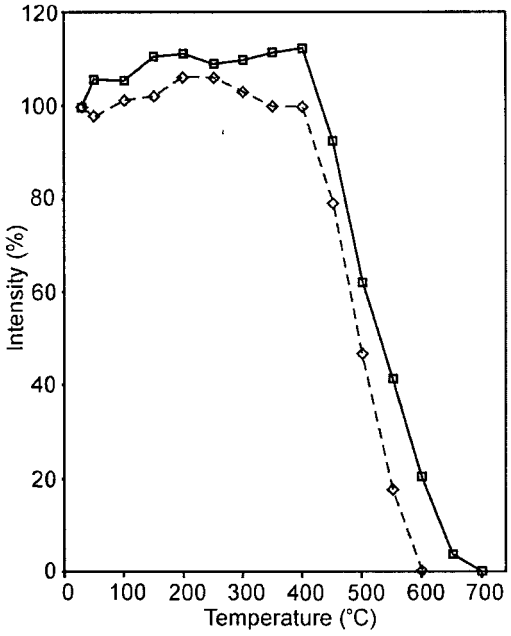

Fig. 2: Variation of the intensity of the basal reflection of the untreated Maria kaolinite (solid line), 40 hours sonicated (dashed line).

ALTERNATIVE WAYS OF HAZARDOUS WASTE TREATMENT FROM PETROLEUM INDUSTRY IN CROATIA

DURN, G.,[1] GAURINA-MEĐIMUREC, N.,[1] VERONEK, B.,[2] MESIĆ, S.,[2] FRÖSCHL, H.,[3] ČOVIĆ, M.[1]

[1] Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb [Rudarsko-geološko-naftni fakultet, Sveučilište u Zagrebu], Pierottijeva 6, Zagreb, 10000, Croatia
[2] Ina-Naftalin, Šubićeva 29, Zagreb, 10000, Croatia
[3] ARC Seibersdorf Research GmbH, Seibersdorf, 2444, Austria
E-mail: gdurn@rgn.hr

Part of the technological waste produced in petroleum industry in Croatia is hazardous waste. Such kind of waste is treated with lime and through processes of stabilisation-solidification it transforms into poorly soluble-inert material which is then deposited in central oilfield pits. Stabilisation-solidification with lime is world-wide used as a technique of treatment of organic and inorganic technological waste. Foreign experiences showed that by usage of this technique for treatment of organic technological waste, or waste with organic and inorganic pollutants, sufficient reduction of pollutant movement in the environment is not caused. Due to this fact, one has to be careful in its application.

The new techniques of treatment are being developed for materials which contain organic or inorganic and organic pollutants. The aim of this research was to examine alternative ways of treatment of technological waste from petroleum industry. The sample of technological waste from central oilfield pit Vinkovci was treated in laboratory conditions with application of single material or application of material combinations: (a) cement, (b) organophilic clay, (c) calcined Moler clay, (d) lime + organophilic clay + bentonite, (e) cement + organophilic clay + bentonite, (f) lime + calcined Moler clay and (g) cement + calcined Moler clay. The sample of technological waste treated with lime was used for comparison of results. The following parameters were determined in treated samples: (a) total oils, (b) mineral oils, (c) polycyclic aromatic hydrocarbons (16) and (d) heavy metals and potentially toxic elements (10). The content of stated parameters is determined in original samples and their destilled water leachates.

The most successful treatment for majority of parameters was treatment with organophilic clay. Such treated sample releases, for example, 63 times less total oils, 67 times less mineral oils, 798 times less naphthalene and 136 times less lead than sample treated with lime. The organophilic clay, as the most successful material, is followed by calcined Moler clay. The obtained results clearly show that reduction of hydrocarbons content with some of the field acceptable ways and detailed chemical analysis of left organic and inorganic pollutants has to be done before the selection of the best method for treatment of technological waste in petroleum industry. Depending on results of analysis, hazardous technological waste can be treated more effective by application of more suitable materials (e.g. organophilic clay) which reduce pollutant release from such treated waste in the environment. In this way the problem of permanent disposal of treated waste can be solved.

GREEN CLAY MICAS IN MAGMATIC ENVIRONMENTS: PRELIMINARY RESULTS IN NORTH HUNGARY

FEHÉR, B.

Department of Mineralogy, Herman Ottó Museum [Ásványtár, Herman Ottó Múzeum], Kossuth u. 13., Miskolc, 3525, Hungary
E-mail: feherbela@axelero.hu

Green clay micas (i.e. glauconite and the celadonite family) occur sporadically in volcanic rocks of the Mátra and Tokaj Mountains, North Hungary. These minerals are associated mainly with Tertiary andesites and rhyolites in the Recsk Andesite (Eocene, Priabonian stage), Hasznos Andesite (Miocene, Karpatian stage), Mátra Andesite (Miocene, Badenian stage) and Tokaj Volcanite (Miocene, Badenian to Pannonian) Formations. Kubovics (1963; 1964a; 1964b) was the first to describe green clay mica as glauconite from Miocene andesite of the Ágasvár Hill, Mátra Mountains, later it was redefined as celadonite (Kubovics, 1966).

In magmatic environments green clay micas occur in three forms: 1) cavity fillings of volcanic rocks; 2) films covering fissures of volcanic rocks and 3) pigment materials in chalcedony or opal. The three forms are different from one another in separability and the quantity of separable material (Table 1). Separation procedures of magmatic green micas

Table 1: Forms of magmatic green clay micas and their separability

Form	Separability	Quantity of separable material
nest	high	large
film	high	small
pigment	low	large (but contamined)

are not as difficult as described in the case of sedimentary glauconites by Fekete et al. (2003). Nest-like clay micas were separated from the host rock by crushing, after which the mineral could be readily hand-picked from the debris. From thin films the mineral can be picked using a sharp needle (cf. Buckley et al., 1978). It is impossible to separate the pigment green clay micas from the host materials (usually opal and chalcedony) so we have to study them together.

In the Mátra and Tokaj Mountains opals and chalcedonies are frequently coloured to green. Green colour is caused by different clay minerals, commonly micas and smectites (nontronite) as well as X-ray amorphous phases. Green colour of opals and chalcedonies proved to be caused by green clay micas at Bábakő, Tolcsva; Veresvíz mine and Kánya Hill, Telkibánya; Bőr Hill, Hollóháza; Cink Hill, Erdőhorváti; Mulató Hill, Erdőbénye; Recsk; Köves Hill, Gyöngyöstarján localities. Weak reflections and frequent absence of the diagnostic 060 peak from the XRD pattern make the identification of the green clay micas mixed with silica difficult. Causes of weak reflections are probably the low degree of crystallinity of micas and/or their very small crystallite size. Therefore some of the X-ray amorphous green phases may be micas with very low crystallinity and/or very small crystallite size. Otherwise silica is very useful in genetic aspect, because it preserved the transformation (oxidation) fronts between green clay mica and iron-oxide (-hydroxide) minerals (hematite, goethite).

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THE MINERAL COMPOSITION OF RED CLAYS IN HUNGARY

FEKETE, J., CSIBI, M.

Department of Soil Science and Agrochemistry, Szent István University [Talajtani és Agrokémiai Tanszék, Szent István Egyetem], Páter Károly u. 1., Gödöllő, 2103, Hungary
E-mail: jfekete@fau.gau.hu

Red clays in Hungary are the products of soil forming processes of Tertiary period and so were not covered by marine sediments.

Basic soil investigations and mechanical analysis (Fekete et al., 1997) were carried out on the red clay samples (Fekete and Stefanovits, 2002; Fekete, 2002). X-ray diffraction and (derivatographic) thermal analysis were applied to determine the mineral composition of the samples by G. Bidló and P. Kovács-Pálffy.

On the basis of soil and mineral analysis these red clays can be rank in various groups:

Red clays in Transdanubia are:

1. The red soils of western periphery of Hungary:

a) Red soils of Kőszeg Hill. Most of the red clays are in situ old ferralitic formations.

b) Red soils of Őrség. We can find decomposed siallitic and rather old ferralitic residuum.

2. Red soils formed on Permian sandstone. It doesn't contain kaolinite and hematite, but contains goethite.

3. Bauxitic formations of Transdanubian medium high mountains:

a) Red clays in which the allite association is dominant. These soils contain high amount of boehmite, gibbsite and kaolinite.

b) Bauxitic red clays which show allitic characteristics. The amount of kaolinite and chlorite is prominent.

4. Red clays of Transdanubian Hill:

a) The red clays have been produced by weathering of Pannonian surface. We can find illite, chlorite, montmorillonite and kaolinite.

b) Red clays of Mecsek and Villányi Hill. These terra rossa formations are in the fissures of limestones.

Red clays of Northern Mountains are:

1. The red clays of Tokaj Foothills, formed on rhyolite tuff with low contain of kaolinite and 40% of montmorillonite.

2. The red soils of Cserehát and Szalonna Hills with high percentage of montmorillonite have a typical red and yellow red colours.

3. The red soils of Aggtelek Karst, Torna Hills and Bódva Valley with 40% of montmorillonite and 10% to 40% of kaolinite.

4. The red soils of Bükk Mountains with very low kaolinite contain, the percentage of illite contain is around 20% and with the very little percentage of montmorillonite.

5. The red soils of Northern periphery of the Great Hungarian Plain with significant amount of montmorillonite have a 10% to 20% of kaolinite.

Micromorphological features of clays are summarised as follows.

The speckled and granostratied b-fabric of the groundmass, whose occurrence is mainly due to swelling and shrinking, were observed in samples from the sites as follows: Gödöllő, Gyöngyöstarján, Hatvan–Gombos, Jósvafő, Kakasd, Kővágószőlős, Mád, Mátrakeresztes, Muzsla, Salgótarján, Szekszárd, Szurdokpüspöki and Valkó. Swelling was confirmed by the occurrence of stress coatings in the red clays from Jósvafő and Szurdokpüspöki.

Occurrences of clay coatings in samples of sites in Gödöllő, Hatvan–Gombos, Kővágószőlős, Mád, Muzsla, Mátrakeresztes, Salgótarján, Szurdokpüspöki and Valkó were interpreted as a micromorphological features of illuviation. The most illuviation coatings and infillings were observed in samples from Hatvan–Gombos and Kővágószőlős. Concerning micromorphological investigations thanks are due to Géza Szendrei for helping.

Acknowledgements

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ACID-ACTIVATED SMECTITE AND GLAUCONITE (LUBLIN AREA, POLAND): TEXTURAL PROPERTIES AND ADSORPTION OF β-CAROTENE

FRANUS, W.,[1] DERKOWSKI, A.,[2] FRANUS, M.,[1] NOWACKI, T.[3]

[1] Department of Geotechnics, Lublin University of Technology [Katedra Geotechniki, Politechnika Lubelska], Nadbystrzycka 40, Lublin, 20 618, Poland

[2] Institute of Geological Sciences PAS [Instytut Nauk Geologicznyh PAN], Senacka 1, Kraków, 31 002, Poland

[3] Department of Road Building, Lublin University of Technology [Katedra Budownictwa Drogowego, Politechnika Lubelska], Nadbystrzycka 40, Lublin, 20 618, Poland

E-mail: ndderkow@cyf-kr.edu.pl

Tertiary clays and sandstones, occurring abundantly in the Lublin area (Poland) contain high amounts of glauconite and smectite (Gazda et al., 2001). The present study was undertaken in order to check the influence of acid activation of clay minerals separated from these rocks on their textural properties and bleaching potential.

Clay minerals, separated by sieving (< 63 μm for smectite-glauconite material) and magnetically (glauconite, from > 63 μm fraction), were activated using 10% HCl or 20% H_2SO_4 at 371°K(±2K), during 1 to 7 hours of reaction, with solid–liquid ratio of 0.067 g/ml. Raw and activated clays were analysed for their mineral and chemical composition (XRD and SEM observation with EDS system). Their physicochemical properties were determined: cation exchange capacity (CEC)—using Mn^{2+} ions desorbed with 1M CH_3COONa solution, as well as specific surface area (BET), specific volume of micropores and specific volume and surface of mesopores—applying argon gas adsorption-desorption in the liquid nitrogen (77°K) temperature (Gregg and Sing, 1982). The content of Mg, Fe and Al elements were analysed in all samples with ICP-AES. The bleaching capacity of tested materials was determined by mixing 1 g of activated material with 40 ml of crude rapeseed oil at the constant temperature of 373°K during 20 minutes. The bleaching potential was estimated based on colour changes of treated oil (mixed with acetone 1:3), measured spectrometrically (Christidis et al., 1997).

The applied acid activation affects the studied clay minerals structures to variable degree. None of applied acids can provoke significant structural alteration of glauconite, only coherent dissolution of whole crystals was observed, incongruent because of silica precipitation. The smectite structure decomposition (observed as 001 XRD reflection degradation) takes place faster than glauconite dissolution. HCl solution applied in the experiments is more aggressive than H_2SO_4 and causes immediate dissolution of smectite, leaving glauconite in fine fraction. 7 hours is needed for smectite dissolution with H_2SO_4.

The textural properties of tested fractions have been significantly improved by activation. The specific surface of the coarse material increases from 78.4 to 324.1 m^2/g after 7 hours of HCl activation and from 85.9 to 236.0 m^2/g for the fine fraction material. The CEC values of glauconite (16.82 meq/100g) and fine fraction (33.17 meq/100g) decrease with acid activation time, due to the dissolution of swelling phases.

The effect of adsorption of β-carotene from rapeseed oil by the tested materials depends on the type of acid applied in the process of their activation. The most advanced bleaching (95%) was found using the sample of fine fraction material after 7 hours reaction with H_2SO_4. Activation by HCl—a more aggressive reagent—results in lower bleaching capacity and confirms the suggestion of "overactivation" (Srasra and Trabelsi-Ayedi, 2000). The produced material can be considered as a high quality bleaching earth.

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REMEDIATION OF SOILS FROM RADIOACTIVE CONTAMINATION

FROST, R. L.

Inorganic Materials Program, School of Physical Sciences, Queensland University of Technology, POB 2434, Brisbane, Queensland, 4001, Australia

E-mail: r.frost@qut.edu.au

Soils have been contaminated with radionucleides in Australia and other parts of the world through the testing of atomic weapons and through mining. Significant contamination exists in the USA. Leaching from tailings dams can contaminate soils through long distances as the radionucleides may be transported through the soils via groundwaters. Such contamination is difficult to remove. The addition of phosphates and the formation of autunites may offer a mechanism for removal of the radioactive contamination. This group of minerals is "clay-like" and has been termed the uranyl micas. These minerals are secondary minerals and are formed from solutions. The implication of such a phenomenon is that the minerals are soluble and will pass into groundwater systems and hence will be transported long distances. This provides the reason for the remediation of soils. Autunite solid-state and solution chemistry plays one of the most important roles in the actinide chemistry, mineralogy, geochemistry and "environmental chemistry" with regard to uranium(VI) migration in natural waters. Actinide autunite complexes inclusive those of uranium are to be reflected in migration from a nuclear waste repository or in accidental site contamination. To gain an understanding of the geochemical behaviour of such materials, a fundamental knowledge of actinide carbonate chemistry and mineralogy seems to be needed (Clark et al., 1995). The study of the uranyl carbonates has been undertaken for an extended period of time (Huang and Kerr, 1960; Neumann and Bryn, 1958). There are a significant number of compounds containing the uranyl ion (Whittle, 1955). Contaminated wastes may also offer a source of radionucleides for terrorism and hence the easy detection of such uranyl minerals is imperative and leads to a new branch of chemistry which might be titled "Nuclear Forensics".

The autunite group of minerals are tetragonal uranyl arsenates, phosphates and vanadates. The minerals have a general formula $M(UO_2)_2(XO_4)_2{\cdot}8\text{–}12\ H_2O$ where M may be Ba, Ca, Cu, Fe^{2+}, Mg, Mn^{2+} or ½ (HAl) and X is As, or P or V. The minerals have a layer-like structure (Locock and Burns, 2003). These minerals are often known as uranium micas (Cejka et al., 1985; Cejka et al., 1984). A characteristic features of the minerals is their layer structure in which uranium is bound in uranyl-phosphate layers. The cations and water are located in the interlayer space. The mineral autunite has the formula $Ca[(UO_2)_2(PO_4)]_2{\cdot}H_2O$. Autunite is amongst the most abundant and widely distributed of the uranyl phosphate minerals, yet because of its pseudotetragonal symmetry and rapid dehydration in air, the details of its symmetry and structure are uncertain. The structure contains the well known autunite type sheet with composition $[(UO_2)_2(PO_4)]$ resulting from the sharing of equatorial vertices of the uranyl square bipyramids with the phosphate tetrahedra. The calcium in the interlayer is coordinated by seven H_2O groups and two longer distances to uranyl apical O atoms. Two symmetric independent H_2O groups are held in the structure only by hydrogen bonding (Locock and Burns, 2003). This paper will show the application of electron microscopy, X-ray diffraction and Raman spectroscopy to the identification of the autunite mineral group and other secondary uranyl minerals.

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"MEMORY" EFFECTS OF HYDROTALCITES

FROST, R. L.,[1] ERICKSON, K. L.,[1] KRISTÓF, J.,[2] HORVÁTH, E.[3]

[1] Inorganic Materials Program, School of Physical Sciences, Queensland University of Technology, POB 2434, Brisbane, Queensland, 4001, Australia

[2] Department of Analytical Chemistry, University of Veszprém [Analitikai Kémia Tanszék, Veszprémi Egyetem], POB 158, Veszprém, 8201, Hungary

[3] Department of Environmental Engineering and Chemical Technology, University of Veszprém [Környezetmérnöki és Kémiai Technológia Tanszék, Veszprémi Egyetem], POB 158, Veszprém, 8201, Hungary

E-mail: r.frost@qut.edu.au

The "memory" effects of synthetic hydrotalcite $Zn_6Al_2CO_3(OH)_{16}.4H_2O$ have been studied using hot stage Raman spectroscopy through both heating and cooling in a flow of moist air. Thermal analysis coupled with mass spectrometry was used to complement the spectroscopic results. Hydrotalcites are layered anionic clays which are based on the brucite structure, $Mg(OH)_2$ (Costantino et al., 1998; Frost et al., 2003; Lopez et al., 1996), where a trivalent cation substitutes for some of the divalent cations. The consequent positive layer charge is balanced by the incorporation of anions and water into the interlayer. The resulting mineral has octahedrally coordinated metals, which form sheets. As there is no overall charge, hydrotalcites are quite stable. The general formula for hydrotalcites is: $[M^{II}_{1-x} M^{III}_x. (OH)_2]A^{n-}_{x/n}. mH_2O$; where $0.2 < x < 0.33$ and M = metal, A = anion (Costantino et al., 1998). The interesting properties of hydrotalcites arise when they are calcined; this process removes the interlayer water, interlayer anions, and the hydroxyls. The calcined hydrotalcite is able to reform the original structure when it is exposed to water and anions (Palomares et al., 2004). This is known as the "memory" effect. Thermal analysis (TG) coupled with mass spectrometry (MS) has been used to study a synthetic hydrotalcite ($Zn_6Al_2CO_3(OH)_{16}.4H_2O$). It was found that there are four mass losses which occur up to 300°C. The first three can be assigned to loss of absorbed water, interlayer water and hydroxyls. The fourth mass loss is assigned to loss of carbonate as carbon dioxide. There is a fifth mass loss which occurs at 550°C, which is most likely a loss of oxygen.

A Raman microprobe spectrometer coupled with a thermal stage was used to follow a calcination of ZnAl hydrotalcite (Frost et al., 2004; Frost and Weier, 2004a; Frost and Weier, 2004b). There are three types of OH stretching vibrations which can be seen which are MOH, HOH and HOH---OCO_2. There is an increase in the intensity of the hydrogen bonded water bands as the temperature is increased, while a decrease in intensity of the water bands occurs simultaneously. Only MOH bands remain after 150°C. There are bands of carbonate anions hydrogen bonded to interlayer water at 1077 cm^{-1} and surface OH units at 1060 cm^{-1}. As the temperature is increased, the intensity of the bands of the anion hydrogen bonded to interlayer water decreases in proportion to those hydrogen bonded to the surface OH units. It is proposed that as the interlayer water is removed, the more carbonate anions are forced to bond with the surface OH units. Another band appears at 150°C due to the anion bonded to two OH units, which is caused by the anion being brought into closer contact with the surface.

This paper will present a thermoanalytical and spectroscopic study of the memory effects of hydrotalcites.

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RAMAN SPECTROSCOPY OF IOWAITE AND OTHER NATURAL HYDROTALCITES

FROST, R. L.,[1] ERICKSON, K. L.,[1] KRISTÓF, J.,[2] HORVÁTH, E.[3]

[1] Inorganic Materials Program, School of Physical Sciences, Queensland University of Technology, POB 2434, Brisbane, Queensland, 4001, Australia

[2] Department of Analytical Chemistry, University of Veszprém [Analitikai Kémia Tanszék, Veszprémi Egyetem], POB 158, Veszprém, 8201, Hungary

[3] Department of Environmental Engineering and Chemical Technology, University of Veszprém [Környezetmérnöki és Kémiai Technológia Tanszék, Veszprémi Egyetem], POB 158, Veszprém, 8201, Hungary

E-mail: r.frost@qut.edu.au

Raman spectroscopy has been used to study hydrotalcites including stitchtite, iowaite, pyroaurite, desautelsite. These minerals show "memory effects" in that after the mineral has been completely destroyed, on exposure to air their structures may be restored.

Hydrotalcites, or layered double hydroxides (LDH's) are fundamentally anionic clays, and are less well known than cationic clays like smectites (Hashi et al., 1983; Ingram and Taylor, 1967). The structure of hydrotalcite can be derived from a brucite structure ($Mg(OH)_2$) in which e.g. Al^{3+} or Fe^{3+} (pyroaurite-sjögrenite) substitutes a part of the Mg^{2+} (Frost et al., 2003; Johnson et al., 2002; Kloprogge et al., 2003). This substitution creates a positive layer charge on the hydroxide layers, which is compensated by interlayer anions or anionic complexes (Taylor, 1969; Taylor, 1982). In hydrotalcites a broad range of compositions are possible of the type $[M^{2+}_{1-x}M^{3+}_x(OH)_2][A^{n-}]_{x/n}\cdot yH_2O$, where M^{2+} and M^{3+} are the di- and trivalent cations in the octahedral positions within the hydroxide layers with x normally between 0.17 and 0.33. A^{n-} is an exchangeable interlayer anion (Hansen and Koch, 1995). In the hydrotalcites reevesite and pyroaurite, the divalent cations are Ni^{2+} and Mg^{2+} respectively with the trivalent cation being Fe^{3+}. In these cases the carbonate anion is the major interlayer counter anion. In iowaite the anion is chloride. Normally the hydrotalcite structure based upon takovite (Ni,Al) and hydrotalcite (Mg,Al) has basal spacings of cca. 8.0 Å where the interlayer anion is carbonate. If the carbonate is replaced by sulphate then the mineral carrboydite is obtained. Similarly reevesite is the Ni,Fe hydrotalcite with carbonate as the interlayer anion, which when replaced by sulphate the minerals honessite and hydrohonessite are obtained. If the carbonate is replaced with chloride the mineral iowaite is formed. The mineral iowaite is characterised by infrared bands at 3700, 3674 and 3626 cm^{-1} attributed to Mg_3OH, Mg_2FeOH and Fe_3OH units. Bands are also observed at 3545, 3421, 3281, 3058 and 2769 cm^{-1} and are attributed to the water OH stretching vibration. A similar set of bands is observed in the infrared spectrum of synthetic pyroaurite. The Raman spectra of the synthetic iowaite are characterised by bands attributed to $(CO_3)^{2-}$ at 1376, 1194 and 1084 cm^{-1}. No bands were observed in these positions for the natural iowaite. The Raman spectrum of natural iowaite shows three bands at 708, 690 and 620 cm^{-1} and upon exposure to air, two broad bands are found at 710 and 648 cm^{-1}. The Raman spectrum of synthetic iowaite has a very broad band at 712 cm^{-1}. The Raman spectrum of natural iowaite shows an intense band at 527 cm^{-1}. The air oxidised iowaite shows two bands at 547 and 484 cm^{-1} attributed to the $(CO_3)^{2-}$ ν_2 bending mode. Raman spectroscopy has proven most useful for studying the chemistry of the hydrotalcite iowaite.

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ORGANO-MONTMORILLONITES FOR THE PURIFICATION OF WATER

FROST, R. L.,[1] XI, Y.,[1] HE, H.,[1] KRISTÓF, J.,[2] HORVÁTH, E.[3]

[1] Inorganic Materials Program, School of Physical Sciences, Queensland University of Technology, POB 2434, Brisbane, Queensland, 4001, Australia

[2] Department of Analytical Chemistry, University of Veszprém [Analitikai Kémia Tanszék, Veszprémi Egyetem], POB 158, Veszprém, 8201, Hungary

[3] Department of Silicate and Materials Engineering, University of Veszprém [Szilikát- és Anyagmérnöki Tanszék, Veszprémi Egyetem], POB 158, Veszprém, 8201, Hungary

E-mail: r.frost@qut.edu.au

One of the major problems facing modern society is the lack of pure water. Many water storage systems are contaminated by a) microbiological and pathological organisms, b) organic molecules, c) toxic anions and d) heavy metals. One method of purification of the organic molecules which may include pesticides, herbicides, PCB's, is to adsorb the organic impurities on a hydrophobic filter. Organoclays which are formed through the ion exchange of the interlayer cation with a cationic surfactant form suitable hydrophobic filters. In this work we present detailed studies of the synthesis, characterisation and application of organoclays.

A detailed observation about the ordering conformation of hexadecyltrimethylammonium (HDTMA) ions confined within the montmorillonite interlayer in different concentration surfactant modified organo-montmorillonites has been obtained by X-ray diffraction, thermal analysis, SEM-TEM and spectroscopic techniques. Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and X-ray diffraction (XRD) have been used to provide new insights into the interlayer structure and morphology of $HDTMA^+$–montmorillonite hybrids (He et al., 2004). XRD patterns show that thermal treatment has an important effect on the stability of the surfactant intercalated in the hybrids, reflected by the significant changes of the basal spacing. TEM and SEM micrographs demonstrate that the hybrids with lower surfactant packing density are mainly composed of irregular layer stacking with a number of curved hybrid layers, while those with higher surfactant packing density are mainly composed of regularly interstratified and flat layers. The variation of the interlayer distances exists in all hybrids and is more obvious in the hybrids with lower surfactant packing density. This study demonstrates that not only the arrangement model of surfactant but also the morphology of hybrid strongly depend on the surfactant packing density within the montmorillonite gallery. X-ray diffraction has been used to study the changes in the surface properties of a montmorillonitic clay through the changes in the basal spacings of montmorillonite (SWy–2) and surfactant-intercalated organoclays. Variation in the d-spacing was found to be a step-function of the surfactant concentration. High resolution thermogravimetric analysis (HRTG) was used to study the thermal decomposition surfactant modified SWy–2-MMTs modified with the surfactant octadecyltrimethylammonium bromide. High resolution thermogravimetry shows the decomposition takes place in four steps. A mass loss step is observed at room temperature and is attributed to dehydration of adsorption water. A second mass loss step is observed over the 87.9 to 135.5°C temperature range and is also attributed to dehydration of water hydrating metal cations such as Na^+. The third mass loss occurs from 178.9 to 384.5°C and is assigned to a loss of surfactant. The fourth mass loss step is ascribed to the loss of OH units through dehydroxylation over the 556.01 to 636.35°C temperature range.

Many studies show that with the increase of the concentration of surfactant, the arrangement of surfactant in the clay interlayer will vary from lateral-monolayer, lateral-bilayer, paraffin-type monolayer and last to paraffin-type bilayer. In this study, the ordering conformation depends strongly on the concentration of the confined amine. In the sample with low amine concentration, the amine ions are parallel to the interlayer and individually separated (Dickey and Carron, 1996). The interaction among amine molecules is very weak. This dilution effect causes the formation of gauche conformers. However, with the increase of the amine concentration, increased interchain interaction and restriction of the room for the movement of the amine tail will be resulted. This will lead to the increase of the number of the ordered conformers which are reflected by the wavenumber shift to lower wavenumber and the decrease of the band width. For the paraffin-type model of the amine chains, there is a relative high packing density. This means the room for movement of the tail of amine chain is limited and the confined amine chains adopt an essentially all-trans conformation. Therefore, there will be no dramatic change of the wavenumber of the bands as demonstrated in the present study. It shows that both wavenumber and band width of antisymmetric and symmetric stretching modes are sensitive to the ordering conformation of the inserted organic surfactant cation. In addition, comparing with that of symmetric stretching mode, the wavenumber of the antisymmetric stretching mode is more sensitive to the mobility of the tail of amine chain.

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QUANTIFICATION OF SMALL AMOUNTS OF SWELLING MINERAL, SMECTITE, IN SYNTHETIC MIXTURES WITH KAOLINITE USING DIFFUSE REFLECTANCE INFRARED SPECTROSCOPY (DRIFTS)

GEDDES, J., BREEN, C., YARWOOD, J.

Materials Research Institute, Sheffield Hallam University, Howard St., Sheffield, S1 1WB, UK
E-mail: jill.geddes@student.shu.ac.uk

Processing problems associated with the presence of low quantities of smectite in kaolinite are caused by the difference in surface area between the non-swelling kaolinite (15–30 m^2/g) and swelling mineral, smectite (700–850 m^2/g). This surface area issue is a problem for the coatings industry, and for reservoir rock analysis. In the oil industry, treatment fluids are pumped into reservoir rocks to increase well productivity. Interactions of this treatment fluid with swelling minerals on the pore surface may catastrophically alter the fluid composition.

The aim of this study was to determine low quantities (0.1–30wt%) of swelling mineral, smectite, in mixtures with non-swelling mineral, kaolinite, using DRIFTS and the chemometric technique, partial least squares (PLS). A third component, calcite, was included in the training set to avoid collinearity. Infrared spectroscopy and in particular, DRIFTS, is an effective technique to determine small quantities of these minerals since it is a sensitive, fast and relatively inexpensive technique. PLS is a decomposition technique which carries out the simultaneous decomposition of spectral and concentration data to construct a calibration model (Clegg, 1998; Forsyth, 2001). It was thought that PLS could improve the detection limit determined by (Madejová et al., 2002) using peak fitting. For a smectite-kaolinite mixture (Madejová et al., 2002) could detect kaolinite at levels as low as 0.5wt%, while smectite could not be detected below 40wt%.

A quantitative determination of components in mixtures was obtained using two software programs and the results compared. OMNIC® software and Spectracalc software package GRAMS® (Galactic Industries Corporation, NH, USA) were used. The most accurate models for the set, containing 21 standards in this study, do not include the OH stretching region, but instead use only the wavenumber region below 2150 cm^{-1}.

The training set was then exposed to a chemical probe, dimethylformamide (DMF). A chemical probe is an organic molecule that easily enters the interlayer space of smectites but much less easily into kaolins. When a mineral mixture or rock is exposed to the chemical probe, the interactions of the molecules with different clay minerals are exploited to detect the clay mineral content. Therefore, a probe was used with the expectation that more accurate quantitative results would be obtained regarding the quantities of different minerals in a mixture. It was thought that the presence of the peak at 1658 cm^{-1}, assigned to intercalated DMF, would improve the models predictive ability. However the peak was found to be present in the spectra of both smectite and kaolinite after exposure to DMF and its presence actually reduced the accuracy and precision of predictions.

Spectra of the training set, without DMF exposure, were then collected using ball milled KBr diluent and a sample compaction device. It was thought that the smaller particle size distribution and homogeneous compaction would improve model predictions. The model produced using this method did give the most accurate predictions.

Results indicate that the highest error in kaolinite prediction is ±2.2%, in smectite is ±3.8%, and in calcite is ±4.9%. In conclusion, it has been found that smectite can be detected at lower concentrations (0.2wt%) using PLS than can be detected visually (30wt%) from a peak on a spectrum, with an error of ±3.8wt%.

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IS CLAY ESSENTIAL FOR THE MANUFACTURING OF CONSTRUCTION CERAMICS?

GOMES, C. S. F.

Centro de Investigação Minerais Industriais e Argilas, Universidade de Aveiro, Campus Universitário de Santiago, Aveiro, 3810 193, Portugal

E-mail: cgomes@geo.ua.pt

Clays are currently used in the manufacture of construction ceramics and other types of ceramics, essentially due to their plasticity, a property that is specific of clay minerals. Plasticity is developed through the clay minerals–water interaction and it allows the workability of the ceramic pastes, which is fundamental for the wet shaping of the ceramic products. However, the fabrication of any clay-based ceramic products is not possible if the clay exclusively consists of clay minerals. In such conditions the body shape is disrupted during drying and firing due to uncontrolled body retraction related to the excessive loss of both free and hygroscopic water. Quartz, mica, feldspar, other silicates and sometimes calcite, existing in the natural clay or added to the clay, can provide the adequate temper of the mixtures.

Slip casting, extrusion and pressing are the most currently used types of ceramic processing. The last two processes can be used in the manufacture of construction ceramics. Extrusion requires a blend of raw materials in the form of paste, what means that for the shaping of the ceramic bodies at least one of the raw materials has to show adequate plasticity.

On the other hand, pressing requires raw materials in the form of almost dry powder, plasticity being not a relevant property for shaping the ceramic bodies, and using high pressure presses of these days, ceramic bodies characterised by high intergranular cohesion can be produced.

Clays—as most of the geologic products—are not renewable resources, and in many regions the currently mined clay deposits are close to the exhaustion. This problem is aggravated since the exploitation of some other potential deposits is not possible due to legal, environmental or territorial planning constraints.

Other geologic materials, such as, phyllites and low grade metamorphic schists of pelitic composition, also have to be considered as ceramic raw materials as replacements of clay deposits. Like in the clay deposits, different silicates, particularly phyllosilicates, are the main components of these geomaterials. The difference concerns the coarse-grain size and the higher mica and chlorite content exhibited by both phyllites and low grade metamorphic schists, as well as the higher density or compaction exhibited by these rocks. Even when finely ground these materials perform very low plasticity. On the other hand the ceramic products manufactured with them are characterised for the low rectraction they exhibit during drying and firing.

Studies on the potential use of phyllites and schists for the manufacture of construction ceramics, particularly floor tiles and massive facing bricks, have been carried out in recent years. Also, fine-grained silty or clayey soils, either residual or redeposited, can be used as raw materials to manufacture construction ceramics. The viability of the production of construction ceramics using mixtures based essentially on low-plastic or non-plastic raw materials, such as residual soils (andosols), lapilli and mud from the processing of aggregates derived from volcanic rocks has been assessed and the results are herewith disclosed and discussed.

MOISTURE EXPANSION OF CONSTRUCTION CERAMICS DUE TO INCOMPLETE HIGH TEMPERATURE REACTIONS

GOMES, C. S. F.,[1] COROADO, J.[2]

[1] Centro de Investigação Minerais Industriais e Argilas, Universidade de Aveiro, Campus Universitário de Santiago, Aveiro, 3810 193, Portugal

[2] Centro de Investigação Minerais Industriais e Argilas, Instituto Politécnico de Tomar, Tomar, 2300, Portugal

E-mail: cgomes@geo.ua.pt; jpfc@ipt.pt

Moisture expansion of clay-based ceramics diminishes both the quality and the durability of the manufactured products due to critical changes on certain physical properties, such as: dimension, shape and intergranular cohesion of the ceramic bodies.

As a matter of fact, moisture expansion as an irreversible phenomenon is a real problem of paramount importance in the ceramic industry. It presently appears to be much more aggravated due to the non-compliance of clay paste composition and texture during the drying and firing processes which are becoming increasingly faster.

Moisture expansion causes negative economic consequences expressed on losses of both quality and durability of the ceramic products.

After drying and before firing moisture reabsorption diminishes the energy of the physical bonds that have been established between the mineral grains of the ceramic raw materials on the dried ceramic body. Moisture reabsorption promoting the formation of water films around mineral grains and the penetration of water into the intergranular pores, represents a reverse process compared to the one that promotes the approximation and establishment of good contacts between individual particles or particle aggregates due to the effect of drying.

After firing, moisture reabsorption and the subsequent expansion of the ceramic body takes place as well, however in a slower rate, and it is most certainly related either to mineral composition, or to the adopted firing cycle, or to both factors. In what mineral raw materials are concerned, moisture expansion, essentially and in theoretical terms, is the result of the reactivity with water and consequent rehydration of both cryptocrystalline metaphases and glass being produced during firing, due to: 1) incomplete transformation of minerals to stable crystalline phases; 2) glass formation derived, either from the structural breakdown of clay minerals, or from the partial fusion of certain components of the ceramic pastes.

In the firing process, moisture expansion, essentially and in theoretical terms, is controlled by the following factors: 1) short duration of the firing cycles; 2) short residence time of the ceramic bodies at the maximum firing temperature.

The firing temperatures of the studied facing bricks made from illitic and carbonate bearing clays were within the range 850–900°C. At these temperatures the evolution of structural water, in the form of (OH) from mica-illite was found to be incomplete, as it could be demonstrated by both differential thermal analysis (DTA) and X-ray diffraction (XRD) analysis. Also, the CaO formed from the decomposition of calcite did not fully reacted with SiO_2. In what concerns the assessment, in terms of quality decay due to moisture expansion, some relevant properties, such as, water reabsorption, and mechanical resistance to flexion and compression, were determined on ceramic test bodies, after drying and after firing.

MINERALOGICAL AND GEOCHEMICAL PROPERTIES OF THE VOLCANIC MUD PRODUCED IN THE FUMAROLIC FIELD OF FURNAS LAKE, SÃO MIGUEL ISLAND, AZORES

GOMES, C. S. F.,[1] SEQUEIRA, C.,[1] TERROSO, D.,[1] ROCHA, F.,[1] GOMES, V.,[2] SILVA, E.,[3] PATINHA, C.,[3] FORJAZ, V.[3]

[1] Centro de Investigação Minerais Industriais e Argilas, Universidade de Aveiro, Campus Universitário de Santiago, Aveiro, 3810 193, Portugal

[2] Departamento de Biologia, Universidade de Aveiro, Campus Universitário de Santiago, Aveiro, 3810 193, Portugal

[3] Centro de Investigação Evolução Litosférica e do Meio Ambiental de Superficie (ELMAS), Universidade de Aveiro, Campus Universitário de Santiago, Aveiro, 3810 193, Portugal

E-mail: cgomes@geo.ua.pt

Alongside the northwestern bank of the "Lagoa das Furnas", in São Miguel Island, Azores archipelago, there is a small area locally called "Caldeiras" that corresponds to a fumarolic field.

The local ground is relatively hot being used as a natural kitchen, where cooking is performed burying pots of food properly closed in the earth at depths estimated at 1 m, approximately. The main traditional meals in this manner prepared is the famous "cozido" that consists of mixed meats (pork and veal) and vegetables, and the also famous "caldeirada de peixe" that consists of mixed varied types of fish.

From the fumarole vents, hot springs, whitish smokes and dark greyish mud are profusely produced.

The hyperthermal waters are highly acidic and the mud is assumed to be the result of the secondary alteration of rocks, mainly of trachytic composition, making the volcanic dome that fills the Furnas caldera. This caldera has derived from the collapse of the Furnas stratovolcano.

The trachytic dome that was grown and built over a main vent has been submitted to thorough alteration, providing as end products, either whitish masses enriched in opaline silica or greyish muds enriched in clay minerals, particularly kaolin minerals.

The present paper deals with both the mineralogical and chemical investigation of the mud referred to. X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses, using Philips diffractometer and spectrometer respectively, have been carried out on samples of bulk mud and of clay fraction.

Bulk mud is composed of kaolinite, alkali feldspar, alunite, calcite, marcasite and opal-A. On the other hand, the clay fraction of the mud consists of the same minerals, differing particularly by its higher kaolinite content.

In terms of chemical composition the bulk mud sample is characterised as follows: SiO_2 40.51%; Al_2O_3 19.75%; TiO_2 1.27%; Fe_2O_3 2.72%; MnO 0.05%; MgO 0.58%; CaO 0.29%; Na_2O 1.93%; K_2O 2.78%; P_2O_5 0.38%; SO_3 4.77%; LOI 25.49%.

Within the trace chemical elements the following deserve particular mention: Zr 1528 ppm; Ba 448 ppm; Sr 29 ppm; Zn 18 ppm; Sn 17 ppm; As 5 ppm; Pb 19 ppm; Cu 9 ppm; Ni 13 ppm; Co 6 ppm; Cr 72 ppm; V 43 ppm.

Also, mud grain size distribution has been assessed on the analysed samples using X-ray based grain size analyser, Sedigraph 5400. The extremely fine-grained mud is characterised by the following granulometric parameters: 100% and 30% of the particles exhibit e.s.d. less than 60 μm and 2 μm, respectively; modal diameter 7 μm; median diameter 4.5 μm. The specific micromorphological features of the mud particles were observed and recorded using scanning electron microscopy (SEM).

CHARACTERISATION OF SOME KAOLINS USED FOR PRODUCING ELECTRIC INSULATOR CERAMIC

GOREA, M., KRISTÁLY, F.

Babeş-Bolyai University [Universitatea Babeş-Bolyai], Mihail Kogalniceanu 1b, Cluj-Napoca, 400084, Romania
E-mail: mgorea@bioge.ubbcluj.ro

The various types of kaolins as representative raw materials for electric insulator ceramics were investigated in order to establish their influence on ceramics properties, defects and microstructure.

The raw samples were tested by X-ray diffraction (XRD), differential thermal analysis (DTA), and infrared spectroscopy (IR) in order to define their mineralogical composition and structural characteristics.

The thermal treatment of ceramic mixture and raw material was carried out at 1300°C temperature for one hour. The microstructure resulted by firing was studied by optical and electron microscopy. The chemical composition of the crystalline and amorphous phases of the ceramic body was studied by EDAX methods. The processing of the data acquired revealed some inhomogeneity in the microstructure of ceramic body.

It is concluded that the final microstructure, defects and properties of ceramic products are influenced by chemical and mineralogical composition of raw materials. The present impurities (Fe and Ti bearing phases) have great influence on electric properties of the ceramics. The mineral phases present in kaolin deposits have significant role in wet preparing (the presence of smectites increases the plasticity, but also increases the fired shrinkage) of ceramic masses and crystalline phase formation during thermal treatment (poor or well crystallised mullite and cristobalite).

SMECTITIC MINERALS IN MARLS OF THE POLISH FLYSCH CARPATHIANS: CRYSTAL CHEMISTRY AND PROVENANCE

GÓRNIAK, K.

Faculty of Geology, Geophysics and Environmental Protection, University of Science and Technology [Wydział Geologii, Geofizyki i Ochrony Środowiska, Akademia Górniczno-Hutnicza], al. Mickiewicza 30, Kraków, 30 059, Poland
E-mail: gorniak@uci.agh.edu.pl

Marls of different age and lithology occurring among flysch deposits of all tectonic units of Polish part of the Outer Carpathians contain smectitic minerals as dominant clay component. Complicated genesis of Carpathian marls (flysch sediments redeposited into deeper parts of sedimentary basin) is the cause of obliteration of their primary features.

The studies of natural samples and of their separated fractions (< 2 μm and 2–0.2 μm; after removal of carbonates) have shown that in all the representative 24 samples of marls the crystal chemistry of the smectitic minerals is very similar. They are represented by dioctahedral smectitic minerals enriched in magnesium, containing about 90% expandable layers. The Hofmann–Klemen effect confirms the localisation of charge mainly in octahedral layer of this minerals. K-saturation test has shown charge heterogeneities, i.e. the presence of high and low charge layers, whereby the former ones are prevailing. Dehydroxylation temperatures below 600°C and > 650°C indicate that the structure of these minerals consists of *tv* and *cv* layers.

These properties indicate that the parent material of the smectitic minerals occurring in Carpathian marls was volcanic in character. Consequently, the occurrence of marly sediments in the Flysch Carpathians can be related to the periods of tectonic activity within their sedimentation basin.

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THERMAL HISTORY OF PALAEOZOIC SOURCE ROCKS IN WESTERN POMERANIA (NW POLAND): ILLITE-SMECTITE AND VITRINITE REFLECTANCE GEOTHERMOMETERS

GÓRNIAK, K., BAHRANOWSKI, K., GAWEŁ, A., RATAJCZAK, T., SZYDLAK, T.

Faculty of Geology, Geophysics and Environmental Protection, University of Science and Technology [Wydział Geologii, Geofizyki i Ochrony Środowiska, Akademia Górniczno-Hutnicza], al. Mickiewicza 30, Kraków, 30 059, Poland
E-mail: gorniak@uci.agh.edu.pl

Thermal history of Palaeozoic oil and gas source rocks occurring in the Western Pomerania is difficult to reconstruct mainly due to fault block tectonics resulting from its position near the Teisseyre–Tornquist line. Dinantian sedimentation basin is considered to represent the back arc basin, periodically intensely supplied with volcanic material, being the source of primary occurring smectite mineral. Consequently, the illite-smectite geothermometer (illitisation of smectite) was used in this study. The Dinantian series is a slope-lagoonal sequence rich in organic matter. Therefore, it enables the application of organic geothermometer (vitrinite reflectance).

As follows of the present studies, the thermal maturity of the rocks studied is variable, depending on the depth of burial of individual tectonic blocks. The results obtained by both geothermometers are compared for the Kołobrzeg and Drzewiany blocks, situated differently with respect to Teisseyre–Tornquist line. Illitisation of smectite for the Drzewiany block and coalification degree of organic matter are lower than for the Kołobrzeg one. The content of expandable layers in mixed layer illite-smectite from Drzewiany block amounts, on the average, to cca. 15% what indicates medium-stage diagenesis, whilst for Kołobrzeg one it is below 10%, corresponding to late-diagenetic stage. Similar conclusions result from the measurements of vitrinite reflectance, amounting to cca. 0.74% for the Drzewiany block and cca. 0.86% for the Kołobrzeg one.

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MICROFABRIC OF MUDROCKS: OBJECTIVE MEASUREMENT AND CLASSIFICATION

GÓRNIAK, K.,[1] SZYDLAK, T.,[1] RATAJCZAK, T.,[1] MLYNARCZUK, M.[2]

[1] Faculty of Geology, Geophysics and Environmental Protection, University of Science and Technology [Wydział Geologii, Geofizyki i Ochrony Środowiska, Akademia Górniczno-Hutnicza], al. Mickiewicza 30, Kraków, 30 059, Poland
[2] Strata Mechanics Research Institute PAS [Instytut Mechaniki Górotworu PAN], Reymonta 27, Kraków, 30 059, Poland
E-mail: gorniak@uci.agh.edu.pl

Mudrocks microfabrics are diverse and this diversity is the effect of sedimentation environment and of the processes taking place in sediment before, during and after burial. In the case of hydrocarbon source rocks the fabric analysis is of practical importance.

In these study procedures were applied enabling simple and rapid measurement of ordering of the rock expressed as the mode of arrangement of its clay and non-clay components (mainly quartz, mica and carbonate grains, as well as fragments of carbonised organic matter). To obtain a complete picture of rock fabric, the spatial distribution and particle to particle relation as well as the size and shape of pore space were also measured.

Seven samples of mudrocks were selected for model studies, showing qualitatively distinctly differing fabric. These samples represent rocks of different age from Lower Carboniferous to Tertiary. They were formed in different sedimentary environments: continental (fluvial, lacustrine) and marine (shelf facies and sediments redeposited from shelf). They are characterised by similar of different composition of clay minerals, grains of coarser fractions than clay, carbonate content and advancement of diagenetic processes. Two of them are considered to represents hydrocarbon source rocks.

The studies were carried out on three preparations from the fragments of rocks: thin sections for optical microscopy, standard SEM preparations and polished samples for SEM-BS investigation. In elaborating the pictures fixed on microphotographs the mathematical morphology methods were used accessible in the APHELION program.

These studies resulted in the proposal of quantitative scheme of classifying the fabric observed in optical and electron microscopy (SEM and SEM-BS).

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MINERALOGY AND GEOCHEMISTRY OF PANNONIAN-PONTIAN PELITIC SEDIMENTS OF THE HRVATSKO ZAGORJE, CROATIA

GRIZELJ, A.,[1] KOVAČIĆ, M.,[1] PAVELIĆ, D.,[1] TIBLJAŠ, D.[2]

[1] Institute of Geology [Institut za geologiju], Sachsova 2, Zagreb, 10000, Croatia

[2] Faculty of Science, University of Zagreb [Prirodoslovno-matematički fakultet, Sveučilište u Zagrebu], Horvatovac bb, Zagreb, 10000, Croatia

E-mail: agrizelj@igi.hr

The aim of the study was mineralogical and geochemical characterisation of the Upper Pannonian and Lower Pontian pelitic (marl) deposits. The Miocene deposits from Hrvatsko Zagorje represent the southwestern margin of the Pannonian Basin and the Central Paratethys realm.

Researches included: X-ray diffraction analysis and chemical analysis of insoluble rock residue and < 2 μm fraction of this residue, modal analysis of silt size fraction, as well as oxygen and carbon isotope analysis in carbonate component. Preparation of the samples for X-ray diffraction analyses of clay included dissolution of carbonate with ammonium acetate buffer (pH = 5), separation of the <2 μm fraction according to Stoke's law and preparation of the oriented aggregates of clay minerals. The X-ray diffraction in oriented aggregates was performed on air-dried, and ethylene glycol treated material, as well as on material heated to 400°C and 550°C. The quantitative analyses were made according to procedure described by Schultz (1964).

1. The proportions of clay minerals and other phases like calcite, quartz and feldspars are very variable. Dominant minerals in investigated rock are calcite (31–74%), quartz (5–21%), feldspars (1–5%) and clay minerals (18–50%), some samples also contain dolomite and pyrite. In the < 2 μm fraction smectite (3–76%), illite (23–72%), chlorite (1–25%) and kaolinite(?) occur. Clay minerals are essentially detrital, most probably derived from surrounding Alps and Carpathian areas, and deposited from suspension in deep lake environment. According to the mineral content all samples are classified as marl or silted marl. Observed mineral composition of marls is in accordance with the results for Miocene pelitic sediments of the Great Hungarian Plain given by Viczián (2002). Apart from that no systematic change in mineral composition was observed in rocks of different ages.

2. The carbonate constituents were determined as calcite and low magnesium calcite (1–5% MgO). Calcite probably precipitated from solution, and suggest warm climate. Gradual shallowing took place in investigated area in the Pontian time as a result of progradation of clastic systems in the south–southeastern direction (Kovačić et al., 2004). It is reflected by increased terrigeneous siliciclastic material and decreased calcite content.

3. Dominant constituents in silt size fraction are quartz, feldspars, rock fragments (chert, quartzite and schists) and micas. Chlorite, limonite, pyrite, garnet, tourmaline, zircon, epidote and staurolite are present in small amounts. Composition of silt size fraction is comparable with the results of modal analysis for Upper Miocene sands from Hrvatsko Zagorje (Kovačić, 2004). According to Kovačić (2004) the results suggest Alpine and possibly Carpathian provenance, too.

4. Observed differences in chemical composition are primarily due to changes in proportions of silt and clay fractions.

5. The results of oxygen and carbon isotope analysis are compared with results for the Miocene from Mátyás et al. (1996) and Geary et al. (1989). According to the results in the Pannonian and Pontian the temperature was app. 20°C and the climate was humid.

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GEOCHEMISTRY OF ILLITE-SMECTITE FROM BURIED BENTONITES OF THE EAST SLOVAK BASIN

HONTY, M.,[1] ŠUCHA, V.,[1] CLAUER, N.[2]

[1] Department of Geology of Mineral Deposits, Comenius University [Katedra ložiskovej geológie, Univerzita Komenského], Mlynska dolina G, Bratislava, 84215, Slovakia

[2] Centre de Géochimie de la Surface, 1 rue Blessig, Strasbourg, 67084, France

E-mail: honty@fns.uniba.sk

K-Ar dating, major and trace element chemistry of the illite particles were studied to elucidate the geochemical changes accompanying the illitisation of buried bentonites in the East Slovak Basin. K-Ar dating of different grain-size fractions containing illite crystals, provided that they are free from detrital contamination, could be indicative of the basin thermal and tectonic history as well as of the illite particles growth history. The narrow and old ages for the different grain-size fractions of the buried bentonites in the marginal parts of the East Slovak basin reflect rapid tectonic subsidence and early uplift. The larger range and younger ages for the same fractions were observed in case of the bentonites coming from the central part of the basin. They suggest slow burial and little or no uplift of the area. In bentonites with long-term illitisation process the variations in K-Ar ages could be used to deduce the illitisation mechanism. The onset of the illitisation process was recorded in the uppermost core of the borehole Čičarovce 1 (%S = 90%), giving zero ages. Decreasing ages with decreasing fraction size probably indicate the dominant role of the nucleation and growth mechanism in the early stage of the illitisation process. The opposite trend could be assigned to the dominant role of the surface controlled growth at the final stages of the illitisation. Our experimental results are in a good agreement with the modelling approach given by Środoń (2002).

The negative linear correlation between Al_2O_3 and SiO_2 contents with the illitisation advancement shows the grade of Al substitution for Si in the tetrahedral sheets. The same trend being observed between Al_2O_3 and MgO suggests in turn the substitution in the octahedral sheets. The mobility of V and Sc in the zone of diagenesis seems to be related with the degree of illitisation.

Finally, REE mobilisation and fractionation was clearly documented in samples from the zone of diagenesis. Systematic decrease of total REE content with decreasing clay size fraction indicates that REEs are not fixed in the clay crystal structure. Positive Eu anomaly is always connected with intensive illitisation and REE enrichment. However, the relationship between REEs and illite-smectite crystals is not yet clearly understood.

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THE ORIGIN OF FINELY CRYSTALLINE MICA FROM PODZOLS, TATRA MOUNTAINS, POLAND: PRELIMINARY RESULTS

JACHER, K.,[1] SKIBA, M.,[1] BANAŚ, M.[2]

[1] Institute of Geological Sciences, Jagiellonian University [Instytut Nauk Geologycznyh, Uniwersytet Jagielloński], Oleandry 2a, Kraków, 30 063, Poland

[2] Institute of Geological Sciences PAS [Instytut Nauk Geologicznyh PAN], Senacka 1, Kraków, 31 002, Poland

E-mail: skiba@geos.ing.uj.edu.pl

Finely crystalline mica is a common constituent of clay (< 2 μm) fractions from different soil types. It is widely accepted that it is mostly of inherited origin (e.g. Środoń, 1999; Wilson, 1999 and literature cited therein). The mica could also be deposited in soil environments as an airborne dust (e.g. Šucha et al., 2001). Soil illitisation was also suggested but not proved by many authors (e.g. Środoń, 1999 and literature cited therein) and wetting and drying in most cases is suggested as the possible illitisation mechanism. Smectite illitisation was systematically studied in laboratory conditions by Eberl et al. (1986). It was concluded that except for basic conditions it consists in reorientation of smectite layers from turbostratic to semi-ordered. According to Środoń (1999; 2003 personal communication) soil illitisation remains still one of the unsolved problems of clay mineralogy. Formation of illite in podzols from the Tatra Mountains was suggested by Oleksynowa and Skiba (1976).

This paper presents preliminary results of the research into the origin of finely crystalline mica from the podzol profile developed in the Tatra Mts. The studied weathering profile was selected because of its relatively high mica content and clear geological and mineralogical background. The profile consist of the podzol which is developed on the older weathering crust formed by physical disintegration during the Pleistocene. In the profile seven soil horizons were distinguished (OFH, OH, AE, Bhfe, Bs, Bs-C, C). Bulk soil samples as well as the separated clay fractions (< 2 μm and < 0.2 μm) were analysed with the use of XRD, FTIR and SEM-EDS methods. Optical microscopy observations of the parent rocks and K-Ar dating of the selected fractions were also performed. The amount of clay fraction measured after the Jackson treatment vary from approximately 8% in the lowest C horizon to near 15% in the upper albic E horizon. The clay fractions composition is typical of the Tatra podzols developed from the crushed or disintegrated tonalites with inherited chlorite, dioctahedral and trioctahedral micas present in the lower soil horizons and dioctahedral micas, mica/expandable and kaolinite occurrence in the upper soil horizons. The upper albic E horizon of the soil studied is relatively rich in dioctahedral micas. SEM-EDS observations indicates that most of the mica grains show the morphology typical for inherited micas with corrosion gulfs and frayed edges. The presence of fibrous like forms with the chemical composition close to Fe-illite which overgrow biggest mineral grains may indicate mica crystallisation from the soil solution. The fibres are < 0.2 μm. The K-Ar data obtained from the < 0.2 μm albic horizon fraction gave the age near 152 Ma which is much younger than 310–320 Ma obtained for tonalite primary micas (biotite and muscovite). The data is probably connected with the presence of the mixture of the older inherited primary mica and the younger mica. The younger mica may be of the soil origin as well as it may be inherited from sericite and secondary muscovite which was observed in the parent tonalite. The possibility of its aeolian origin have to be also considered. The origin of finely crystalline mica from the podzol studied remains unclear. Further investigations including detailed SEM-EDS observations as well as K-Ar dating of the soil, aeolian deposited mica and different generations of secondary mica from crystalline rocks are needed.

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CHEMICAL RESISTANCE OF CEMENT-BENTONITE SUSPENSION FOR SLURRY CUT-OFF WALL

JANOTKA, I., KRAJČI, Ľ.

Institute of Construction and Architecture SAS [Ústav stavebníctva a architektúry SAV], Dúbravská cesta 9, Bratislava, 84503, Slovakia
E-mail: Ivan.Janotka@savba.sk

In Europe, bentonite occurrence in large quantities and high quality in Greece, Italy, Spain, Great Britain, Cyprus, Bulgaria, Hungary, Romania, Czech Republic and Slovakia is known. Most of deposits belong to open-cast mining and contain Ca-montmorillonite as the main component. The Ca-bentonite can be transferred to Na-type for utilisation in finished products for a very broad range of industrial applications. Until recently, exclusively sodium bentonite has been used in practice. The most important properties of sodium bentonite are high specific surface area (the very small particles compared to e.g. cement), high swelling capacity, the cation exchange capacity and low permeability. Bentonite is therefore a unique clay mineral with very high swelling potential and water adsorption capacity.

Cement is a system composed of clinker minerals and gypsum that react with water at different rates giving hydration products of various composition and crystallinity. Type and volume of the formed hydration products influence porosity, strength and other engineering properties of hardened final product. The use of only Portland cement generates some undesirable problems with shrinkage-expansion behaviour, chemical resistance and durability of cement composites. To this end, much attention in recent years is devoted to the development of new generation cements with the aim to improve physical-mechanical properties, chemical and environmental resistance, non-permeability and durability of final products. However, these cements are mainly suitable for concrete making technologies. The next idea (appeared approximately 50 years ago) was to get a synergetic effect by a combination of swelling (sodium bentonite) and non-swelling minerals (cement) for specific construction techniques (vertical barriers known as slurry cut-off walls). It is known that the first cut-off walls were built in the USA in 1945 having 12 m depth and 1.20 m thickness. In the present days slurry cut-off walls reach depth 20–30 m up to 60 m and vary in thickness between 0.6 and 1.2 m. Generally, two main production techniques are known for slurry cut-off walls: two-phase and one-phase method. The two-phase method is based in the first step on the bentonite suspension only that fills and stabilises the excavated trench. It is replaced in the second step by the concrete. This method is rather time-consuming, laborious and expensive. Therefore it was tried to replace two steps by the only one based on filling up the trenches by one sealing material. For this aim the bentonite suspension was mixed with cement during excavation for stabilisation of the trench. After excavation, the cement-bentonite suspension stayed in the trench creating after hardening permanent casting and sealing element.

The technological requirements on the cement-bentonite suspension for slurry cut-off walls are: stability and homogeneity after mixing with water having suitable viscosity (flow ability measured by the Marsh cone) and low water decantation. The claim to be achieved is to manufacture a cement-bentonite suspension that stays workable and flow able during the excavation period of several hours without any separation effects having in the final effect sufficient mechanical properties and chemical resistance. It is of great importance because compressive strength of cement-bentonite suspensions varies between 0.1 and 1 MPa up to 2 MPa. This is due to high water to cement ratios (1 to 3 and more). Sufficient chemical resistance is an essential requirement for slurry cut-off walls. This is caused by the fact that statistical reviews have found that more than one half of subsurface waters have aggressive effect on the hardened cement-bentonite suspension. Moreover, in the case of slurry cut-off wall deterioration, the protected surrounding will suffer by the hazardous chemical substances.

This paper shows the results of the chemical resistance of the cement-bentonite suspension with adjusted flow ability (Marsh test varies between 42 s and 45 s), water decantation less than 2vol% per 24 hours of suspension sedimentation in 1 litre cylinder and having 28-day compressive strength of 0.5 MPa. The suspension consisted of blast furnace slag Portland cement CEM II / A–S 32.5 (cement plant Povazska cementaren, a.s. Ladce) and sodium bentonite from Jelšový Potok deposit delivered as the final product Bentovet K (Gemerská nerudna spoločnosť, a.s. Hnusta), both from Slovakia. The suspension mixture composition on 1 m^3 is: 323 kg of cement, 27 kg of Bentovet K and 885 l of water (water to cement ratio = 2.74). The suspension was prepared by activated mixing to comply as much as possible with ready-mixed suspensions on the construction sites. The basis for the use of testing of aggressive solution is given in STN 73 1215 Concrete Structures—Classification of Aggressive Environments. It is worthy to mention that the published criteria in the above Standard are valid for concrete only and not for cement-bentonite suspensions having compressive strength ten to hundred times lower compared to concrete. No Standard related to cement-bentonite suspensions has been issued until now in the world. The chosen aggressiveness modified with regard to these facts represents the combined chemical attack of magnesium, chloride, ammonium and sulphate ions contemporarily. Long-term resistance of the suspension is described and assessed as well as cement-bentonite interaction and microstructure development of the specimens kept in reference water or exposed to aggressive medium are discussed too.

LOW-TEMPERATURE METAMORPHISM OF MOUNT MEDVEDNICA (CROATIA): PHYLLOSILICATE CHARACTERISTICS VERSUS ORGANIC MATURITY

JUDIK, K.,[1] RAINER, T. M.,[2] TIBLJAŠ, D.,[3] RANTITSCH, G.,[2] SACHSENHOFER, G.,[2] ÁRKAI, P.[1]

[1] Laboratory for Geochemical Research HAS [MTA Geokémiai Kutatólaboratórium], Budaörsi út 45., Budapest, 1112, Hungary
[2] Department Angewandte Geowissenschaften und Geophysik, Montanuniversität Leoben, Peter-Tunner-Str. 15, Leoben, 8700, Austria
[3] Faculty of Science, University of Zagreb [Prirodoslovno-matematički fakultet, Sveučilište u Zagrebu], Horvatovac bb, Zagreb, 10000, Croatia
E-mail: judik@geochem.hu

Recently, several authors focused on the reconstruction of the structural evolution of the border zone of the Alps, Dinarides and the Pannonian Basin (e.g. Haas et al., 2000). Mount Medvednica represents one of the largest southwestern outcrops of this border zone, i.e. the Zagorje–Mid-Transdanubian Zone.

In this study we are dealing with the metamorphic evolution of three tectonostratigraphic units of Mount Medvednica listed here from the bottom to the top: the Middle Jurassic-Early Cretaceous ophiolitic mélange, the Palaeozoic complex and Late Cretaceous-Palaeocene overlying sequence (Pamić and Tomljenović, 1998) using coal rank (vitrinite reflectance), X-ray powder diffraction (XRPD) based characterisation of the fine dispersed carbonaceous materials and for comparison, phyllosilicate "crystallinity" indices (illite Kübler and chlorite Árkai indices), apparent mean crystallite thickness and lattice strain data obtained by the Voigt method and chlorite empirical Al(IV) geothermometers.

Random, maximum and minimum vitrinite reflectance and bireflectance data were measured on organic material (OM)-rich phyllite, slate and shale samples from the three studied units. Maximum reflectance values (R_{max}) of phyllite samples from the Palaeozoic complex vary between 6.88% and 9.76%, minimum reflectance (R_{min}) data fall in the range of 1.26–2.33% providing bireflectances from 4.81 to 7.85%. These values indicate meta-antracite–semi-graphite stages corresponding to epizonal conditions exceeding 300°C. Selected dispersed OM-rich samples from the Palaeozoic complex were prepared for XRPD studies in order to determine the 002 peak position and the height/full width at half height dates of the organic material. According to Landis (1971) the measured peak positions (3.35–3.36 Å) correspond to the graphite-d_1 stage in the graphite-d–graphite series. Graphite-d_1 stage records temperature below 400°C, but requires at least greenschist facies, chlorite zone conditions. These data compared to illite Kübler and chlorite Árkai indices, crystallite thickness and lattice strain values and to temperature data obtained by the chlorite Al(IV) geothermometers underline high temperature anchizonal–epizonal conditions falling in the range of 300–400°C.

Random vitrinite reflectance values of shales from the Jurassic-Cretaceous ophiolite mélange and from the Cretaceous-Palaeocene complex are cca. 2.15% and 1.6%, respectively. These data agree fairly well with the illite Kübler and chlorite Árkai indices, crystallite thickness and lattice strain values, which prove conditions corresponding to the late-diagenetic zone and transitional between the diagenetic and anchizones.

Organic maturity data compared to phyllosilicate "crystallinity", crystallite thickness and lattice strain results are complementary tools to determine metamorphic conditions of fine-grained siliciclastites containing no diagnostic, facies indicating mineral assemblages.

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GEOLOGY, MINERALOGY AND THE USE OF THE BENTONITE CLAYS (PËRRENJASI, ALBANIA)

JUSUFATI, M., GRAZHDANI, E.

Albanian Geological Survey [Shërbimi Gjeologjik Shqiptar], 153 rr. Kavajes, Tirana, Albania
E-mail: Jusufati2000@yahoo.com

Përrenjasi bentonite ore deposit is situated in the southwestern part of Albania. It is located in the Quaternary (Holocene) sediments of the Përrenjasi graben structure, which is surrounded by the Middle Jurassic ultramafics, Upper Jurassic-Cretaceous flysch, Upper Cretaceous limestones and Middle Oligocene flysch. The Quaternary deposits are composed of two main sequences: 1) lake-alluvial sediments (Q_{3-4}^{l-al}) (clays containing pebbles of varying composition, intercalated with small silt, sand and gravel layers); 2) alluvial-proluvial sediments (Q_4^{al-pr}) (gravels, sands and clays). The productive bentonite layer is found in the upper part of the second sequence. It is covered by a thin humus layer. The clay deposit is several hundred m long and 4 m thick. It is relatively homogeneous, but locally silty and sandy layers are also recognised. The clays are of brownish to black, greyish to dark grey colour. They are soft, plastic, and greasy and soap like to the touch and have swelling capacity.

The Quaternary deposits of the Përrenjasi graben are considered of the lacustrine-alluvial-marshy origin. The area is inferred a semi-closed basin with only slightly perturbed sedimentation regimen. The ultrabasic rocks, carbonates, gneisses, acid magmatic pebbles of Oligocene conglomerates, basic volcanics, and various sedimentary rocks are the source rocks leading to the formation of the basin sequences.

Prospecting geological works are carried out for the clay deposit assessment. A regular prospecting net 50×50 m and 100×50 m is applied. The hand-made boreholes drillings of 7–16 m depth and 4–5 m deep pits are performed. The works are accompanied by regular sampling. The qualitative evaluation of the clays is made using chemical, mineralogical, X-ray diffractometric, differential thermal analyses.

On the basis of 84 analyses the average chemical composition of the clays is: SiO_2 49.84%, Al_2O_3 7.61%, Fe_2O_3 12.6%, TiO_2 0.49%, CaO 1.52%, MgO 9.025%, Ni 0.2%, Co 0.018%, Mn 0.005%, Na_2O 0.52%, K_2O 0.49%, LOI 17.8%. Average granulometric composition is as follow: gravel 7%, sand 19%, silt 25%, clay 49%. Plasticity number Ip = 26 At, volume weight γ = 1.8 gr/cm^3, Specific weight Δ = 2.2–2.6 gr/cm^3. X-ray diffractometric analyses supplied these data: montmorillonite 65%, illite 1%, kaolinite 4%, quartz 21%, feldspar 1%. The heavy fraction is composed of hematite, magnetite, and ilmenite. The analytical data suggest that Përrenjasi clays belong to montmorillonite group.

The clays are named bentonites because they show the ability to swell in water, to be slaked and activated by acid. They are used mainly to prepare oil and ore deposits well drilling mud. The mixture of 65–98% water and 2–30% clay is the most appropriate one. Some time, small additives are used as well. Another industrial use is their activation with 2–3% Na_2CO_3 and 0.2–0.3 Na(OH) (solution). Generally, these clays are considered as highly active. The local people used the clays as soap, because they indicate good washing properties. At the same time, they are used as cleaning material of general utilisation.

The exploitation conditions are environmentally friendly.

HYDROTHERMAL STABILITY OF COMPOSITES PREPARED FROM METAKAOLIN (GEOPOLYMER) AND SLAG

KOLOUŠEK, D.,[1] VOREL, J.,[1] DOUŠOVÁ, B.,[1] ANDERTOVÁ, J.,[1] KOVANDA, F.,[1] PAŽOUT, R.,[1] BRUS, J.,[2] URBANOVÁ, M.,[2] DROTTNEROVÁ, J.,[3] HOLEŠINSKÝ, R.[3]

[1] Department of Solid State Chemistry, Institute of Chemical Technology [Ústav chemie pevných látek, Vysoká škola chemicko-technologická], Technická 5, Praha, 166 28, Czech Republic

[2] Institute of Macromolecular Chemistry AS CR [Ústav makromolekulární chemie AV ČR], Heyrovsky nam. 2, Praha, 162 06, Czech Republic

[3] Research Institute of Building Materials [Výzkumný ústav stavebních hmot], Hněvkovskeho 67, Brno, 617 00, Czech Republic

E-mail: David.Kolousek@vscht.cz

The amorphous geopolymer structures originate by the reaction of metakaolin and metasilicate of the alkaline metals. Some rise from the mixture of calcined kaolin with the hydroxides of Na or K in the furnace. Fig. 1 presents XRD pattern of the calcined metakaolin with NaOH. It is possible to recognise three mineral phases in this pattern. The first is hydroxisodalite originated from the recrystalisation of thermally alkali activated metakaolin on air and the other two are originally present minerals in kaolin, quartz and mica. The presence of hydroxisodalite or zeolites in the composite materials is an evidence of the origin of the geopolymer matrix. The composite in the form of cube was prepared from thermally activated metakaolin in the environment of NaOH and KOH, slag and an appropriate amount of water. Three sets of experiments were prepared differing in the ratio between metakaolin and slag (the system without the slag, 10:90 and 50:50) without further addition of alkaline to this mixture. The cubes were heated in an oven for 5 hours at 80°C in the plastic foil and 5 hours at the same temperature without the plastic foil. After a period of one week the cubes were either heated at the temperature 100 and 140°C with or without presence of water in the autoclaves for 24 hours and one sample from each series was left to spontaneous ageing. After autoclave treatment and spontaneous period of the ageing the cubes were subjected to the measurement of the mechanical strength, X-ray powder diffraction and selected samples were measured by ^{27}Al MAS NMR and ^{29}Si MAS NMR.

The geopolymer contained in the composite material is rigid (inactive) because sufficient strengths were not attained at temperature of ageing 25°C (Fig. 2). The higher compressive strength in the composites is achieved either by the addition of the suitable binding material (slag) or by the heating of metakaolin in autoclave at 140°C. The amorphous geopolymer changes by the development of higher compressive strength of the composites on the crystalline byproducts namely phillipsite, zeolite X or hydroxisodalite. The "structure" of the geopolymer is changed by fitting silicates Na and K resulting from the dissolution of quartz at 140°C. This process is probably responsible for the development of higher compressive strength of the system. If the system contains 50% of the slag then the compressive strength is as much as 77 MPa after autoclaving cubes at 140°C in the system without H_2O. Phillipsite and hydroxisodalite were detected in both experiments carried out at 140°C. The decreasing alkalinity of the composite system (ratio 10:90) adversely influences compressive strength and as well the dissolution of quartz. At 140°C in the system with H_2O tobermorite crystallises from the CSH gel which originates by the alkaline activation of slag. In addition weak reflections of zeolite X appeared in the pattern. The system of thermally and alkali activated geopolymer with binder is a suitable means of laboratory examination of time-dependent interactions in composites.

Acknowledgements

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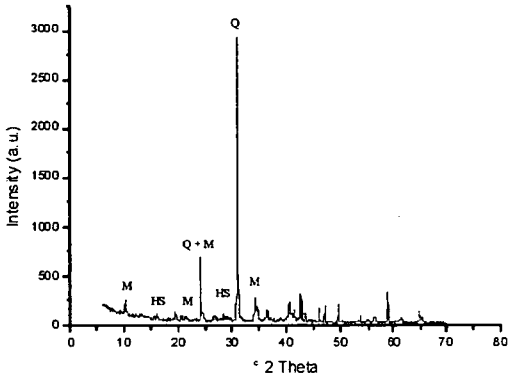

Fig. 1: XRD powder diffraction pattern of calcined kaolin with NaOH

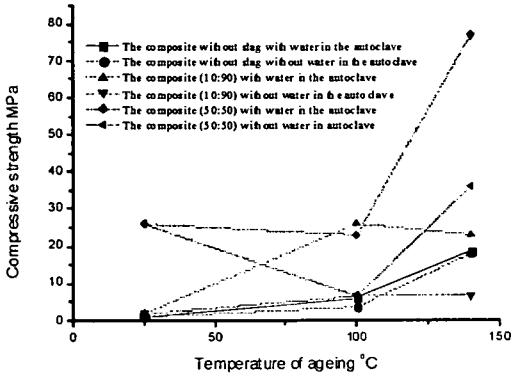

Fig. 2: Compressive strength of composites vs. temperature of ageing for various compositions and treatments of composites

CURRENT KNOWLEDGE ON THE LAYER CHARGE OF CLAY MINERALS

KOMADEL, P.

Institute of Inorganic Chemistry SAS [Ústav anorganickej chémie SAV], Dúbravská cesta 9, Bratislava, 84503, Slovakia
E-mail: uachkomp@savba.sk

Presentations given on the preconference workshop devoted to layer charge, one of the most important characteristics of clay minerals, to be held in Smolenice, Slovakia, on 18 and 19 September 2004, will be summarised.

The invited lectures include:

- cation exchange capacity and layer charge of clay minerals;
- use of the NH_4^+ – IR signal to study the layer charge of clay minerals;
- a new method for determination of layer charge and charge distribution of smectites;
- influence of layer charge on hydration, swelling and cation exchange properties of smectites in aqueous systems;
- structural Fe(III) reduction in smectites;
- charge of component layers in illite-smectite;
- distribution of atomic charges in models of smectite layers;
- the alkylammonium method in the lab: From preparation to calculation of the layer charge of smectite;
- effect of the layer charge of smectites on optical properties of organic dyes;
- critical evaluation of methods of determining layer charge;
- optimising layer charge for sorption, catalysis and composites.

STUDY OF THE CHANGE IN THE PROPERTIES OF Mn-BENTONITE BY AGEING

KOMLÓSI, A., NAGY, N. M., KÓNYA, J.

Isotope Laboratory, University of Debrecen [Izotóp Laboratórium, Debreceni Egyetem], Egyetem tér 1., Debrecen, 4010, Hungary
E-mail: komlosia@tigris.unideb.hu

Clay minerals play a very important role in nature, since they have ability of adsorption and ion exchange. The replacement of the octahedral Al^{3+} by Fe^{2+}, Mg^{2+}, and that of the tetrahedral Si(IV) by Al^{3+} results in negatively charged layers. It is neutralised by the intercalation of exchangeable hydrated cations. There are lots of papers dealing with the structure, properties and reactions of cation exchanged clay minerals. Though many works deal with the reaction of manganese and clays, as far as we know, no work dealt with the ageing of Mn(II)-montmorillonite. The change of the oxidation state of manganese compounds (that is the effect of ageing) was investigated by some workers, but clay minerals were not involved.

Some clays can adsorb different organic substances in the interlayer space, and can catalyse various organic syntheses. Therefore it is very important to study in what extent various cation exchanged montmorillonites can adsorb organic substances. The adsorption of valine on calcium-, copper-, zinc-montmorillonite and montmorillonite KSF was investigated by Nagy and Kónya (2004).

In this work the structure and properties of fresh manganese(II)-bentonite was compared with that of an old substance. It was concluded that the oxidation state of Mn changed during the years. This did not cause many changes in the scanning electron microscope (SEM) and in the X-ray diffraction (XRD) studies; caused minor changes in the Mn-concentration (determined by XRF), thermoanalytical and electron spectroscopy analysis (ESCA). The change in the oxidation state of manganese was highly indicated by the colours of the samples (fresh had a light colour, while the old one was dark brown), the difference in the surface sites, titration curves, redox potentials, adsorption and catalytic activity of the fresh and the old Mn-bentonite. Potentiometric titration data were evaluated by surface complexation model (Davis et al., 1978) using FITEQL3.2 program (Herbelin and Westall, 1996). Stability constants of edge charge reactions, the number of aluminol, silanol and edge sites (X^-) were calculated, and shown in the table below. Potentiometric titration data of commercial and freshly made MnO_2 were also evaluated; the calculated constants and site numbers were compared with that of found in literature. Catalytic and adsorption activity of the samples were also investigated. It was found that fresh Mn-bentonite does not adsorb valine, while the old one and MnO_2 does. Fresh Mn-bentonite does not catalyse the decomposition of H_2O_2, while the old one as well as MnO_2 does.

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Table 1:

	Fresh Mn-bentonite	Old Mn-bentonite	Commercial MnO_2	Fresh MnO_2
logK ($AlOH + H^+ \Leftrightarrow AlOH_2^+$)	7.365	8.092	–	–
logK ($AlOH - H^+ \Leftrightarrow AlO^-$)	–7.184	–8.165	–	–
logK ($SiOH - H^+ \Leftrightarrow SiO^-$)	–5.086	–7.065	–	–
logK ($MnOH + H^+ \Leftrightarrow MnOH_2^+$)	–	4.581	4.266	2.629
logK ($MnOH - H^+ \Leftrightarrow MnO^-$)	–	–7.447	–6.387	–3.331
$[MnOH]_{total}$ (mol/g)	–	$2.69E^{-3}$	$5.193E^{-4}$	$3.49E^{-3}$
$[AlOH]_{total}$ (mol/g)	$2.72E^{-4}$	$1.06E^{-4}$	–	–
$[SiOH]_{total}$ (mol/g)	$2.32E^{-3}$	$1.804E^{-4}$	–	–
$[X^-]_{total}$ (mol/g)	$1.04E^{-3}$	$2.643E^{-4}$	–	–

MIGRATION OF RADIONUCLIDES THROUGH BENTONITE LAYERS

KÓNYA, J., NAGY, N. M.

Isotope Laboratory, University of Debrecen [Izotóp Laboratórium, Debreceni Egyetem], Egyetem tér 1., Debrecen, 4010, Hungary
E-mail: noemi@tigris.klte.hu

A concept for the storage of radioactive and other wastes envisages the use of bentonite layer as buffer material in deep geological disposal. The condition of this application of bentonites is the understanding of the migration processes of radionuclides in bentonite and surrounding geological environment as well. In this presentation the rigorous mathematical solution of the general migration equation is shown for linear radionuclide transport, spatial transport in isotropic and anisotropic medium. All solutions can formally be reduced to the Fick's second law. The adsorption of the radionuclides is also included.

The migration equation for linear transport is checked by migration of Cl–36, Cs–137, and Sr–85 isotopes through bentonite layers.

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QUALITY ACCEPTANCE TESTING OF GCLs FOR LANDFILL APPLICATION

KOVAČEVIĆ ZELIĆ, B.,[1] MATESIĆ, L.,[2] VELICKOVIĆ, B.[1]

[1] Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb [Rudarsko-geološko-naftni fakultet, Sveučilište u Zagrebu], Pierottijeva 6, Zagreb, 10000, Croatia

[2] Geokon Zagreb, Starotrnjanska 16a, Zagreb, 10000, Croatia

E-mail: bkzelic@rgn.hr

"Jakuševec" is the main waste disposal site of Zagreb, the capital of Croatia. As the leachate from the dump may have a negative impact on the city drinkable water supply system, a reconstruction of the dump into a sanitary landfill started few years ago. From the considered alternatives of remediation, it was finally decided to construct the impermeable bottom liner and cover systems, both of which should be made by the usage of natural soil materials and different types of geosynthetics. Geosynthetic clay liners (GCLs) are used within the cover system as a low permeability barrier layer. GCLs are manufactured barriers composed of mineral material (mainly bentonite) and synthetic carriers (different types of geotextiles). The main purpose of GCLs at landfills is to control i.e. to minimise the water infiltration into the waste body. Because of the extremely low hydraulic conductivity, GCLs, although very thin (5–7 mm), are used as a replacement for thick compacted clay liners.

In order to fulfil the requirements for landfill applications, GCLs were subjected to the manufacturing quality control during the production and to the quality assurance procedures at construction site. According to quality assurance testing program at the Jakuševec landfill, mineralogical and physical properties of bentonite component were determined. Testing program consisted of: XRD-analysis, swell index test of clay mineral component of GCL (ASTM D 5890), fluid loss test of clay component of GCLs (ASTM D 5891–95) and water absorption capacity (DIN 18 132).

Swell index (free swell) and water absorption capacity (Fig. 1) are index tests which quantify the swelling property of GCLs mineral component. These test methods are useful for establishing the relative quality of a clay component in a simple and quick way. Fluid loss is a very quick method of determining a bentonite's ability to perform as a hydraulic barrier i.e. to create a seal. A low fluid loss value indicates a low permeability value, too.

Some test results are given in Table 1 for two types of GCLs. By the comparison of prescribed and measured values it can be concluded that these two types of GCLs fulfil, in general, the project requirements.

Table 1: Laboratory test results

Index test	Prescribed values	Measured values	
		Bentomat T–16	Saltex 30
Water adsorption capacity (DIN 18 132)	≥ 450% (Na-bentonite)	410–555	430
Swell index (ASTM D 5890)	> 24 ml	30–34	24–25
Fluid loss (ASTM D 5891)	< 18 ml	10–12	9

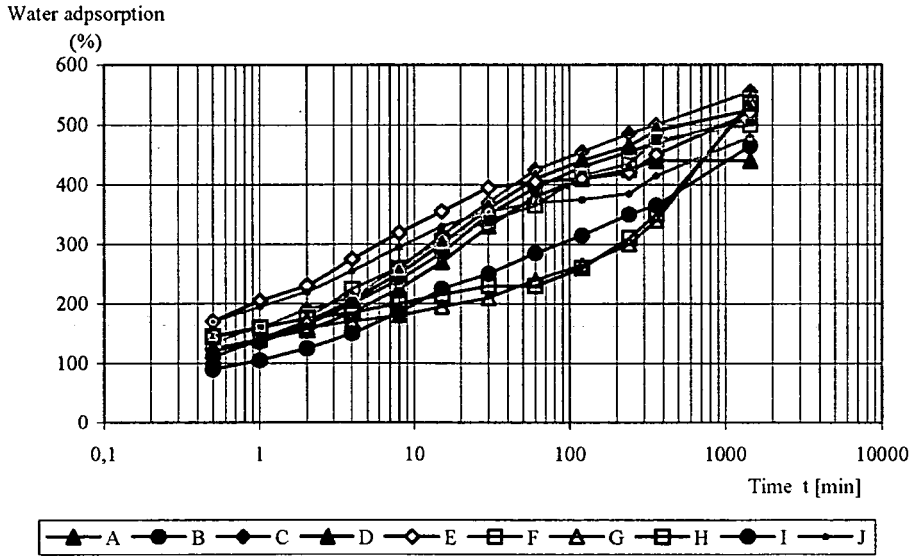

Fig. 1: Water adsorption capacity test results for Bentomat T–16

EFFECT OF THE Ni-Al HYDROTALCITE-LIKE PRECURSOR HYDROTHERMAL TREATMENT ON THE PROPERTIES OF THE RELATED MIXED OXIDE CATALYST

KOVANDA, F.,[1] ROJKA, T.,[1] JIRÁTOVÁ, K.,[2] OBALOVÁ, L.[3]

[1] Department of Solid State Chemistry, Institute of Chemical Technology [Ústav chemie pevných látek, Vysoká škola chemicko-technologická], Technická 5, Praha, 166 28, Czech Republic
[2] Institute of Chemical Process Fundamentals [Ústav teoretických základů chemické techniky], Rozvojová 135, Praha, 165 02, Czech Republic
[3] Department of Physical Chemistry and Theory of Technological Processes, Technical University of Ostrava [Katedra fyzikální chemie a teorie technologických procesů, Technická univerzita Ostrava], tř. 17. listopadu 15, Ostrava–Poruba, 708 33, Czech Republic
E-mail: Frantisek.Kovanda@vscht.cz

The well dispersed homogeneously mixed oxides are formed during thermal decomposition of hydrotalcite-like compounds (layered double hydroxides) and therefore the hydrotalcite-like precursors are often used for preparation of mixed oxide based catalysts. Hydrothermal treatment of the precursors may increase their crystallinity and particle size, depending mainly on temperature and time of the crystallisation process. The layered crystal structure of hydrotalcite-like compounds collapses during the thermal decomposition and the oxides obtained at moderate temperatures are rather amorphous but a relation between the precursor crystallinity and properties of prepared catalysts may be considered.

The Ni-Al layered double hydroxide with Ni/Al molar ratio of 2 was prepared by coprecipitation. The obtained suspension was hydrothermally treated in autoclaves under autogeneous water vapour pressure at 180°C for 4–20 hours. The washed and dried precursors were then formed into extrudates and calcined at 450°C. The prepared precursors and calcined products were characterised by powder X-ray diffraction, scanning electron microscopy, BET surface area and pore size measurements, Raman spectroscopy and temperature programmed reduction. The prepared Ni-Al mixed oxides were also tested in the catalytic decomposition of N_2O.

A hydrotalcite-like phase of relatively low crystallinity was present in the coprecipitated product. Together with hydrotalcite diffraction lines, some slight unidentified diffraction lines were found in the powder XRD patterns of hydrothermally treated samples. The integral intensity and full width in half maximum (FWHM) of diffraction (003) and (006) lines were evaluated to compare the crystallinity of samples hydrothermally treated for various times. The integral intensity of both diffraction lines increased with time of hydrothermal treatment. A significant decrease of FWHM values in a relatively short time (4 hours) was observed, then the time dependence of the FWHM values was less evident. The hydrothermal treatment caused also a decrease in the surface area and porosity of the coprecipitated product. The SEM images showed a considerable increase of crystal size of the hydrothermally treated samples.

Samples calcined at 450°C contained NiO (bunsenite), no other crystalline phases were detected. The XRD patterns of calcined samples showed only a slight difference in the integral intensity of NiO diffraction lines but a gradual decrease of the FWHM values with increasing time of the precursor hydrothermal treatment was observed. The hydrothermal crystallisation of precursors considerably influenced the reducibility of calcined samples. The maximum reduction of the studied mixed oxides shifted to higher temperatures with the time of precursor hydrothermal treatment (from 525°C measured for sample without hydrothermal treatment to 580°C for sample treated for 20 hours). The total H_2 consumption in the temperature interval 20–800°C was nearly the same for all calcined samples but the H_2 consumption measured between 350 and 450°C decreased with time of hydrothermal treatment. On the other hand, the hydrothermal treatment of precursors slightly increased the catalytic activity of obtained mixed oxides in the catalytic N_2O decomposition.

Acknowledgements
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Table 1:

Time of precursor hydrothermal treatment [hour]	FWHM of diffraction lines [°2θ]		H_2 consumption (350–450°C) [mmol H_2/g]	T_{50}* [°C]
	hydrotalcite (003)	NiO (200)		
0	4.083	3.820	0.72	382
4	0.591	3.217	0.29	374
8	0.509	2.679	0.24	378
20	0.393	2.460	0.17	370

* Temperature at which 50% conversion of N_2O was achieved (0.1 g of catalyst, 1000 ppm N_2O in He, flow rate 100 ml min^{-1})

STRUCTURE ELUCIDATION OF KAOLINITE INTERCALATION COMPLEXES BY ADVANCED INSTRUMENTAL TECHNIQUES

KRISTÓF, J.,[1] FROST, R. L.,[2] HORVÁTH, E.[3]

[1] Department of Analytical Chemistry, University of Veszprém [Analitikai Kémia Tanszék, Veszprémi Egyetem], POB 158, Veszprém, 8201, Hungary

[2] Inorganic Materials Program, School of Physical Sciences, Queensland University of Technology, POB 2434, Brisbane, Queensland, 4001, Australia

[3] Department of Environmental Engineering and Chemical Technology, University of Veszprém [Környezetmérnöki és Kémiai Technológia Tanszék, Veszprémi Egyetem], POB 158, Veszprém, 8201, Hungary

E-mail: kristof@almos.vein.hu

Although organoclay complexes occur everywhere in nature, the systematic study of clay-organic interactions started only at the beginning of the last century using mainly X-ray diffraction and DTA techniques (Yariv and Cross, 2002). From the early sixties, simultaneous TG-DTG-DTA analysis (by means of the Derivatograph) opened a new chapter in this field of research.

During the last decades of the century the appearance of highly sophisticated instruments (e.g. TG-MS, FTIR, Raman microscope) contributed enormously to the progress of clay science. This "interdisciplinary" approach offered the possibility of setting up more refined structural models for e.g. intercalation complexes based on the reliable measurement data of complementary nature.

In the present paper the potential of this multi-method approach is demonstrated via the investigation of hydrazine-intercalated kaolinites using XRD, TG-DTG-MS, CRTA, FTIR and Raman microspectroscopy (Kristóf et al., 2002; Horváth et al., 2003; Frost et al., 2002). The continuous monitoring of the gas phase composition, the IR/Raman spectra of the bonded reagent and the host mineral, as well as the diffractometric pattern of the complex as a function of the temperature offers a unique possibility of precise determination of the complex structure. Identification-discrimination of active inner and outer surface sites of different bonding strengths can contribute to the better understanding of clay-organic reactions. With accurate mass loss data, the amounts of differently bonded reagents can be determined. The role of water in the formation of the intercalation complex, in the subtle nature of the decomposition process in different environments, as well as in the understanding of the mechanism of partial collapse and re-expansion can be cleared based on the results of the different spectroscopic analyses.

The reactivity of kaolinite can be improved by mechanochemical activation. With the intercalation and the subsequent thermal deintercalation of mechanochemically treated kaolinite superactive centres can be produced. With this method the properties of surface-modified minerals can be tailored to different applications.

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CLAY MINERALS OF NORWEGIAN SEA (OFFSHORE BEAR ISLAND) SEABED SEDIMENTS AS INDICATORS OF SEDIMENTARY ENVIRONMENTS

KRUPSKAYA, V.

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry RAS [Институт геохимии и аналитической химии им. Вернадского В. И. РАН], Kosygina 19, Moscow, 119991, Russia
E-mail: vi_kru@bk.ru

Integrated geological and geophysical study of seabed sediments of the Bear Island region, southwestern margin of the Barents Sea, allowed to characterise sediments of various types related to the action of hydrocarbon fluids, hemipelagic sedimentation, slope processes and combined influence of all these factors. Relatively homogeneous sediments are subdivided into several sedimentary types based on the grain size distribution. Ratios of clay minerals, as well as their morphological and structural characteristics, are described for each type. Clay minerals include illite, chlorite, kaolinite, smectite, illite-smectite and chlorite-smectite mixed layers.

Hemipelagic sediments are characterised by high illite content (60–70%) and low content of smectite and mixed layer minerals (less than 10%). Hemipelagic interval, characterised by increased silt content (interval B) also had higher content of mixed layer minerals. It is concluded that episode of formation of the interval B coincided with an additional source of material supply probably related to the discharge of ice-rafted material. Such intervals are usually bedded.

According to published data, roots of the Haakon Mosby mud volcano are located at a depth of about 3000 m. From the Pliocene the Bear Island region was receiving sediments formed in the areas of erosion on the Barents Sea shelf and subsequently transported downslope. A major part of the Barents Sea area was dominated by sediments with the illite content higher than 60%. Sediments collected from the mud volcano are characterised by high (40–50%) contents of smectites and illite-smectite mixed layer clay minerals. Mixed layer clay minerals of the illite-smectite series are probably formed as a result of the transformation of illite under the influence of hydrocarbon fluids. Such transformations are thought to take place in sediments affected by mud volcanoes, clay diapirs, and fluid discharge.

The clay mineral composition of sediments collected from different slopes of a local high of unknown origin is very similar to that of hemipelagic sediments including low-density turbidites and probably contourites. Grain size distribution indicates the nepheloid character of sediments. The high appears to be different from other similar structures in the area formed by clay diapirs and is thought to be a headwall of a large submarine slide.

Based on the mixed layer clay minerals (illite-smectite series)/kaolinite ratio, diapiric structures are divided into the smectite (early) and kaolinite (late) generations. The Haakon Mosby mud volcano is related to the late generation.

The obtained results demonstrate that hemipelagic sediments have often undergone redeposition and were incorporated in turbidites and contourites. Redeposited diapiric and hemipelagic material detected in nepheloid sediments suggests that they were derived from slopes of local highs represented by diapirs or structures like slide headwalls.

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COMPOSITION OF CEMENT IN TERRIGENEOUS ROCKS OF VARTOVSKIY ARCH (WEST SIBERIA) AND ITS RELATION TO RESERVOIR PROPERTIES

KRUPSKAYA, V.,[1] KALMIKOV, G.,[2] KHOTILEV, O.[2]

[1] V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry RAS [Институт геохимии и аналитической химии им. Вернадского В. И. РАН], Kosygina 19, Moscow, 119991, Russia

[2] All-Union Scientific Research Institute of Geological, Geophysical and Geochemical Systems, Varshavskoe sh. 8, Moscow, 113115, Russia

E-mail: vi_kru@bk.ru

Rock reservoir properties are particularly important for estimation of reserves of an oilfield and for designing the optimal strategy of its exploration. Porosity and permeability can be estimated by geophysical well logging, core sample analyses and other methods.

Individual grains form a hard framework of cemented clastic rocks which change very little during catagenesis with almost no effect on pore space. Therefore, reservoir properties of the rocks depend mostly on composition of clay minerals, their origin and structure. Thus, knowledge of clay minerals composition and identification of degree and stages of their alterations are very important for understanding reservoir properties of rocks.

Upper Jurassic and Lower Cretaceous rocks of Vartovskiy Arch are represented by arkosic fine-grained sandstones, siltstones with clay cement and bedded silty-clayey rocks. Clay cement always consists of a mixture of illite, chlorite, kaolinite, smectite and mixed layer illite-smectite and chlorite-smectite. Kaolinite and chlorite have significant variations of content and are in negative correlation with each other. Illite and smectite are allogenic and illite-smectites were formed during post-depositional transformation.

Contents of chlorite and kaolinite varied through geological time. Rocks from Upper Jurassic to upper part of Lower Cretaceous are characterised by continuous increase of chlorite content which abruptly decreases by Cenomanian time and kaolinite becomes a dominant clay mineral in Cenomanian rocks. Authigenic clay minerals were formed in several stages. Initially, during catagenesis, chlorite crust was formed. Later, after oil infiltrated the interval, the crust has undergone dissolution with simultaneous formation of kaolinite cementation. Authigenic chlorite and kaolinite were formed in pores of different size and type. Chlorite was forming crusts around grains of fine-grained sandstones and siltstones with smaller pores. The peak of chlorite formation was in Late Valanginian. Allogenic chlorite is also found in small amounts as clastic grains.

Authigenic kaolinite is represented by two types: large, chaotically arranged flakes, infilling the whole pore space and loose vermicular aggregates of up to silt in size. The former type is fund predominantly in small pores of the Upper Jurassic bedded clayey-silty rocks along with authigenic chlorite. These rocks have the worst reservoir properties among the studied formations. The latter type is found mostly in Cenomanian rocks with the minimal chlorite contents. It is thought that the large pore size facilitated almost complete dissolution of the initial chlorite crust and subsequent formation of the vermicular kaolinite aggregates. A mixture of both types is found in Valanginian rocks with medium-size pores and good reservoir properties.

It is generally believed that formation of authigenic chlorite degrades reservoir properties while formation of kaolinite does the opposite. Our study showed that this may not always be the case. Although formation of chlorite does decrease porosity, the permeability may remain the same or even increase. Formation of kaolinite can have both, positive and negative, effects on reservoir properties. It is found that morphology of the kaolinite crystals depends on pore size.

CLAY MINERAL–POLYMER INTERACTIONS: COLLOID CHEMICAL ASPECTS

LAGALY, G.

Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Olshausenstr. 40, Kiel, 24098, Germany
E-mail: h.mittag@email.uni-kiel.de

The colloidal state is an important property in small- and large-scale applications of bentonite dispersions. The clay minerals can be dispersed forming stable sols, coagulated or flocculated in form of more or less dense flocs, or stiffen to gels. Phase diagrams (salt concentration vs. bentonite content) of bentonites in water are characterised by domains of sol, coagulated states, and two types of gels ("repulsive" and "attractive" gels). The addition of polymers provides a simple method to increase or decrease the different domains, i.e. to induce a wanted state (sol, coagulated, flocculated, or gel) at a wanted bentonite content. Examples are given for bentonites in the presence of cationic poly(ethylene oxides) (macromolecules with a cationic charge at the ends). The phase diagrams of the bentonite dispersions reveal increasing steric stabilisation against flocculation by increasing poly(ethylene oxide) addition.

REACTIONS OF ORGANIC MOLECULES WITH SMECTITE SURFACES IN AQUEOUS SYSTEMS

LAIRD, D. A.

National Soil Tilth Laboratory, US Department of Agriculture – Agricultural Research Service, 2150 Pammel drive, Ames (Ia.), 50011, USA
E-mail: laird@nstl.gov

Water is the solvent of ecosystems, and smectites are the most abundant class of clay minerals found in soils and surficial sediments throughout the world. Thus, understanding of chemical reactions between anthropogenic organic molecules and smectite surfaces in aqueous systems is crucial for understanding the fate of pesticides and other organic contaminants in natural environments.

On a macroscopic scale smectites are strongly hydrophilic, however the hydrophobic-hydrophilic character of smectite surfaces varies dramatically on a molecular scale. Basal oxygens proximal to sites of isomorphous substitution carry a partial negative charge and are amenable to polar interactions. These surface charge sites interact with water molecules solvating the charge balancing interlayer inorganic cations. Polar moieties of neutral organic molecules typically are not competitive with water molecules for surface charge sites, and therefore interact with water molecules solvating the inorganic cations. Basal oxygens distal from sites of isomorphous substitution are valence satisfied and are incapable of polar interactions. These hydrophobic nanosites form van der Waals bonds with non-polar moieties of organic molecules.

The net interaction energy between organic molecules and hydrated smectites, hence sorption affinity, depends on the nature, size and distribution of the hydrated interlayer cations, hydrophilic nanosites and hydrophobic nanosites relative to the stereo chemistry of the organic molecules. The surface charge density of smectites is inversely related to the average size of the hydrophobic nanosites and hence the potential contribution of hydrophobic interactions to sorption of organic molecules. Surface charge due to Al for Si substitution in the tetrahedral layers of smectites is highly localised in the three basal oxygens of the aluminate tetrahedra. By contrast, surface charge sites originating from isomorphous substitution in the octahedral layer are spread over about ten basal oxygens. Thus the average size of hydrophobic nanosites is three times larger in tetrahedrally charged smectites than in octahedrally charged smectites with the same surface charge density.

The above model provides a framework for understanding reactions between organic molecules and smectite surfaces. Strongly polar organic molecules, such as pyridine, are not sorbed on smectites from aqueous systems. Pyridine is not polar enough to be competitive with water for salvation of the inorganic cations but it is too polar (lacks a non-polar moiety) to interact with the hydrophobic nanosites. By contrast, weakly polar molecules, such as atrazine and 3-butylpyridine, are sorbed on smectites from neutral aqueous systems. Sorption of weakly polar compounds varies from 0 to 100% depending on the surface charge density and percentage of tetrahedral charge. Non-polar molecules, such as chlorpyrifos and phenanthrene, are strongly sorbed by smectites from aqueous systems. Sorption of non-polar molecules, however, is not correlated with surface charge density or percentage of tetrahedral charge. Furthermore, affinity of smectites for non-polar organic molecules increases with the amount adsorbed, suggesting that such molecules are retained by capillary condensation rather than being sorbed in the interlayers.

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SODIUM BENTONITES: DEFINITIONS AND METHODS FOR DISTINGUISHING SODIUM ACTIVATED AND NATURAL SODIUM BENTONITES

LANDIS, C.,[1] MAUBEUGE, K. von[2]

[1] BPM Minerals LLC, 410 17th St., Suite 405, Denver (Co.), 80202, USA
[2] Naue Fasertechnik GmbH, Wartturmst. 1, Luebbecke, 32312, Germany
E-mail: charles_landis@halliburton.com
E-mail: kvmaubeuge@naue.com

The global bentonite supply chain is now a complicated system of many sources for an even larger number of potential end-use applications. However, the majority of the bentonites consist either of natural sodium bentonites, or naturally occurring bentonite dominated by divalent cations (Ca^{2+} and Mg^{2+}) subsequently modified with sodium cation. The latter variety is often called "sodium activated", or "soda-ash treated" bentonite. Once exchanged with sodium these bentonites are often difficult to distinguish from natural sodium bentonites using common commercial testing protocols. Due to their similar colloidal and bulk chemical properties, the lack of test procedures designed specifically to identify this product feature, and the failure in the industry to completely or effectively explain their differences, sodium activated bentonite quality is often considered to be identical to natural sodium bentonite. This paper defines both general types of sodium bentonite and describes physical and chemical methods that can be used to distinguish these two bentonite types. Specifically, chemical properties such as alkalinity, pH, CO_2 and Na_2O contents, carbon (C^{13}/C^{12}) and oxygen (O^{18}/O^{16}) isotopic ratios, and amounts of water-soluble matter distinguish activated, even slightly activated bentonites from natural bentonites.

STRUCTURAL TRANSFORMATION OF GARFIELD NONTRONITE DURING INTERACTION WITH METALS

LANTENOIS, S.,[1] MULLER, F.,[1] BENY, J. M.,[1] JULLIEN, M.[2]

[1] Institut des Sciences de la Terre d'Orléans, Université d'Orléans, 1a rue de la Férollerie, Orléans, 45071, France
[2] Laboratoire de Modélisation des Transferts dans l'Environnement, Centre CEA de Cadarache, Saint-Paul-lez-Durance, 13108, France
E-mail: sebastien.lantenois@univ-orleans.fr

Smectite-metals interactions have been studied with the aim to predict the reactivity of clayey engineered barriers with the metallic container used for the radioactive waste confinement. Recent results (Lantenois, 2003) have shown that metallic iron reacted in contact with Garfield nontronite to form magnetite. This result has been obtained under acidic pH conditions at 80°C during 45 days. During this reaction, clay sample was not transformed.

In this work we present the results obtained with zinc, cobalt, nickel and magnesium metal after interaction with the Garfield nontronite

$(Na_{0.05}Ca_{0.23}K_{0.01})(Fe^{3+}_{1.86}Al_{0.18}Mg_{0.02})(Si_{3.5}Al_{0.49})O_{10}(OH)_2$.

Experiments have been performed with a 1/2/50 ratio for the clay / metal powder / MilliQ water. The pH of the solutions has been fixed at 5 with HCl added. The mixture has been placed in a Teflon reactor and heated at 80°C during 45 days. After the reaction, solids and solutions have been separated by filtering. Solutions have been analysed by ICP-AES and solid phases have been characterised by XRD and infrared spectroscopy. The results:

• XRD pattern analyses show that nontronite reacted with the metals. Oxides or hydroxides have been identified. A modification of smectite has always been observed: after the reaction, the position of 00ℓ reflections is modified. The 001 reflection shifts from 15.2 Å to 14.4 Å and new 00ℓ reflections appear at ≅ 7.3 Å, 4.85 Å and 3.68 Å. This new phase is not hydrated and has no swelling property with ethylene-glycol.

• FTIR patterns show that OH stretching bands of Garfield nontronite are always present after the reaction. For all metals, OH bands appear between 3625 and 3660 cm^{-1}, they are probably characteristic of the presence of brucitic $M(OH)_2$ layer. These positions are not characteristic of the brucite phase. The localisation of brucite layer in the interlayer space of Garfield nontronite can explain this band.

The results obtained during the interaction between Garfield nontronite and metallic iron are totally different with other metals such as magnesium, cobalt, nickel or zinc.

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THE CLAY "AQUIFER" OF THE "HUNYADI JÁNOS" AND "FERENC JÓZSEF" MEDICINAL WATER

LORBERER, Á. F.,[1] NÉMETH, T.[2]

[1] BABER[2001] Bt., Szentendrei út 19., Budapest, 1035, Hungary

[2] Laboratory for Geochemical Research HAS [MTA Geokémiai Kutatólaboratórium], Budaörsi út 45., Budapest, 1112, Hungary

E-mail: baber@hdsnet.hu

Hungary, and also Budapest is known for being rich in balneological medicinal water. However, in the South part of Buda, there is a special medicinal water, which is bottled and used since the end of the 19th century. This is a bitterish taste laxative water called "Bitterwasser" (German) or "keserűvíz" (Hungarian). In the beginning of the 20th century, six different area was utilised just in the capital for bottling this special high TDS-content groundwater. Two of them is still working. Their trademarks, namely the "Hunyadi János" and "Ferenc József" medicinal water is still represents the mood of the Austro-Hungarian Empire. This "Bitterwasser" is a shallow groundwater, enriched in Na^+, Mg^{2+} and SO_4^{2-}. It is yielded from simple digged wells in two small plain basin situated between the Buda Hills and the Tétényi Highland. The basins are filled by thick Oligocene aged clay layers. In this case, the "aquifer" of the medicinal water is also this compact Kiscell Clay! Geochemical, geophysical end even geothermal anomalies, and special flora is known to be related to this area. The protection area of the wells is one of the few remaining green fields inside Budapest.

The research about the characteristics and the genesis of this "Bitterwasser" was one of the first topic of the Hungarian geologists. The first analyses of the groundwater was made in 1863. The first theory about the origin of this groundwater was constructed by Szabó in 1868. Since than, most of the great Hungarian geologists had some work related to this special groundwater. The theory about the genesis of this groundwater was improved by Schafarzik (1902) and later by Vendl (1948). The most known theory published by Vendl was based on field and microscope description of the clay layers, and also on some chemical analyses. According to our information, there were no modern mineralogical and geochemical studies since that time. Our aim was to reinvestigate the geology and hydrogeology of the area, which work included state-of-art mineralogical and chemical study of the clay layers. In this case, new results about the origin of this special groundwater can take part an important role in the determination of a new protection area.

The clay layers of the mineral water fields are really characteristics. On the surface there is a 10–30 cm thick organic-rich clay. Under this there is a spotted clay: the dominant colour is yellow, with greyish-blue fragments. This clay matrix is full of gypsum, the amount is increasing downwards. Between 2 and 3 m, crystalline gypsum represents about 50% of the material in the central areas of the well-fields. The size of these crystals varies between 1 mm to 3 cm. There is a 30 cm thick dominantly grey, yellow-potted clay layer under 3 m, and then a uniform greyish-blue clay layer begins. We found this basic layer until at least 35 m. The upper part of this layer is also containing some gypsum especially large crystals as fragment fillments.

According to the classical theory, the formation of gypsum and the medicinal water is related to the oxidative process of the unsaturated zone. This is beginning with the production of sulfuric-acid from pyrite. Then the clayey material is decayed by this acid, and gypsum is precipitated as a result of this reaction. The blue-coloured clay represents the original pyrite-rich material, while the upper yellow clay is the oxidated phase. According to this theory the process will be finished when all pyrite of the upper 3 m will be lost. A hydrogeological interpretation (Tóth 1995) states that the basins are recharge areas, so most part of the gypsum is simply exaggrageting from the dissolved content of the upcoming groundwater. We are investigating the validation of both theory, using field measurements and chemical and isotopic analyses of the new samples.

The preparation of the samples was quite difficult in this case due to the high amount of gypsum in the material. We investigated yellow, blue and brown clay samples by XRD, and they were quite similar in mineral composition and oxidative state. We find no sign of pyrite or any other Fe-rich mineral in the samples. There was only one sample from a more sandy layer, in which some goethite could be find. The previous documents mention only dolomite in the material, but we find the presence of calcite is much more important. The dominant mineral of the clay was the smectite in most of the samples.

According to our preliminary results, the classical theory of Vendl cannot be the main process resulting this special situation. The most part of gypsum and the mineral water must be a result of some other, probably more difficult processes.

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TOXIC HEAVY METALS IN THE CLAY MINERALS OF FLOTATION WASTE DUMP OF GYÖNGYÖSOROSZI, NORTHEASTERN PART OF HUNGARY

MÁDAI, V.

Department of Mineralogy and Petrology, University of Miskolc [Ásvány- és Kőzettani Tanszék, Miskolci Egyetem], Egyetemváros, Miskolc, 3515, Hungary
E-mail: askcesar@gold.uni-miskolc.hu

Waste of mining may damage the environment seriously. Rainwater flowing through the waste impoundment with the oxygen from the air oxidises the sulphide minerals of the waste. One of the most reactive components is pyrite (FeS_2), which is the most common ore mineral in the mining wastes. Low pH solutions produced may dissolve other less reactive solid-state minerals. Therefore, the heavy metal content of the acidic solutions may become toxic (Jambor et al., 2000).

These kinds of solutions may be treated in many ways. The pH of the acidic solution can be raised adding lime. Therefore, the toxic heavy metal ions can be precipitated. The effluent solution or the leachate flowing into the groundwater can be stripped by flowing through a reactive barrier. The other way of the treatment is to prevent the oxidation process or to isolate the waste from atmospheric oxygen in the air and water. To reach this aim the upper few cm of the impoundment must be compressed or covered by impermeable clayey layers. Using the metal retention capability of the clay minerals, the environment may also be protected from the toxic heavy metal containing effluents (Hermanns Stengele and Plötze, 2000).

Gyöngyösoroszi is situated in the northeastern part of Hungary, in the Mátra Mountains. The flotation waste impoundment is found upstream of the village. The Gyöngyös Ore Mining Company was established in 1952. The exploited ore was processed on the spot by flotation. After the separation of the lead, copper, zinc and pyrite concentrate, the remaining pyrite-rich tailing was transported by pipeline to the tailing pond. At the end of the 1970s the operation of the mine became unprofitable, and it was closed in 1986 (Fügedi et al.) without properly decomissioning the underground and surface mine facilities, among others the tailing pond.

The environmental hazard of the waste impoundment depends on the mineral assemblages of the waste, the state of the oxidation process of the sulphide minerals. The type and grade of the environmental hazard determines the applicable treatment possibilities.

In this study, the different kinds of clay mineral assemblages of the waste were examined. The metal content of these clay minerals was studied in order to define how to decrease the environmental risk of acid rock drainage. By XRD examinations, montmorillonite, illite-montmorillonite mixed structure minerals, illite, and chlorite were found in the waste material. The contained metals in the clay minerals were determined by EDAX methods.

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BEHAVIOUR OF DIFFERENT CATIONIC FORMS OF MONTMORILLONITE UPON HEATING: AN FTIR STUDY

MADEJOVÁ, J.

Institute of Inorganic Chemistry SAS [Ústav anorganickej chémie SAV], Dúbravská cesta 9, Bratislava, 84503, Slovakia
E-mail: uachjmad@savba.sk

The changes upon heating up to 300 °C in the structure of Jelšový Potok (JP) montmorillonite (Slovakia) saturated with Li^+, Cu^{2+} or Cd^{2+} cations have been investigated. The cation exchange capacities (CEC) of the samples heated to 300°C for 24 hours (Li-JP300, Cu-JP300 and Cd-JP300) decreased to 12, 36 and 74%, respectively, of the values determined for unheated samples (Li-JP, Cu-JP and Cd-JP).

The infrared spectra of Li-JP, Cu-JP and Cd-JP show similar positions of the bands in the middle-IR (MIR, 4000–400 cm^{-1}) and near-IR (NIR, 9000–4000 cm^{-1}) regions. The bands related to the OH stretching vibration ($\nu_{OH} \approx 3628$ cm^{-1}) and OH overtone ($2\nu_{OH} \approx 7070$ cm^{-1}) have been selected as diagnostic for indication of a layer charge decrease and/or for creation of the trioctahedral domains. No significant changes are seen in the MIR spectra of Cd-saturated samples heated below 200°C. Cd-JP requires heating at 250 or 300°C to invoke structural changes. The OH overtone of Cd-JP200 shows no modification in comparison with Cd-JP, however, a shift by 20 cm^{-1} for Cd-JP300 is in accord with the CEC value indicating layer charge decrease.

MIR spectra of Li-JP heated up to 300°C indicate a marked structural alteration of the samples. A gradual displacement of the ν_{OH} band to the higher positions and the appearance of a new component near 3670 cm^{-1} ($\nu_{AlMgLiOH}$) reflect layer charge decrease and fixation of Li^+ in the previously vacant octahedral positions. Similar upward shift and splitting of the $2\nu_{OH}$ overtone into two components at 7170 cm^{-1} and 7100 cm^{-1} is observed in the NIR region. A strong band at 7170 cm^{-1} confirms formation of trioctahedral domains in Li-JP samples heated above 150°C.

The OH stretching region of Cu-JP reveals a shift of the ν_{OH} to 3634 cm^{-1} for Cu-JP200. No further changes occur in spectra of Cu-JP upon heating up to 300°C. The NIR spectrum of Cu-JP300 shows $2\nu_{OH}$ overtone at 7095 cm^{-1}. Unexpectedly, a new component near 7043 cm^{-1} has appeared in the spectra of the samples heated above 150°C. Presence of Cu(II) in the octahedral sheet is one possible explanation. If Cu^{2+} enters the previously vacant octahedral sites then the most probable grouping would be AlMgCuOH. Based on the IR data published for other clay minerals, the estimated position of $2\nu_{AlMgCuOH}$ overtone should be near 7110 cm^{-1}. This position, however, is over 60 cm^{-1} higher as the band observed at 7043 cm^{-1}. It follows that the assignment of the 7043 cm^{-1} band to $2\nu_{AlMgCuOH}$ is doubtful. Moreover, the EPR spectroscopy revealed that Cu(II) in Cu-JP300 can be partially coordinated by oxygen atoms from the mineral layers and by nitrogen atoms from pyridine molecules, if present in the interlayers (Karakassides et al., 1999). Both IR and EPR spectra suggest that Cu^{2+} cations are fixed deep in the hexagonal cavities close to OH groups. The H^+–Cu(II) interaction can influence both the length and orientation of OH dipole and thus also the vibrational frequency of the OH group. However, the possibility to attribute the 7043 cm^{-1} band to the existence of isolated clusters formed by Cu^{2+} and water molecules in the interlayers of smectites upon heating cannot be excluded.

Different location of Li(I) and Cu(II) in heated JP montmorillonite has activated the question whether small Li^+ ions can migrate into the vacant octahedral sites after Cu(II) has been trapped in the hexagonal cavities. Therefore, the exchangeable Cu^{2+} ions from Cu-JP200 were exchanged by Li^+ and the obtained sample was heated at 300°C to evoke fixation of Li^+ (Li(Cu)-JP300). No band indicating a presence of Li(I) in the octahedra is visible in the MIR spectrum. However, the NIR spectrum clearly shows three bands in the OH overtone region. In addition to the bands at 7102 and 7048 cm^{-1}, found also in the Cu-JP300 spectrum, a band at 7166 cm^{-1}, present at similar position in Li-JP300, has been identified. This band unambiguously confirms fixation of Li^+ in the octahedral positions of the Li(Cu)-JP300.

Analysis of the IR spectra reveals that both the size and the charge of interlayer cations affect their final position after fixation upon heating. The Li^+ ions migrate into the octahedral vacancies, thus creating local trioctahedral domains. Although ionic radius of Cu^{2+} is comparable to that of Li^+, Cu(II) is retained in hexagonal cavities of heated Cu-JP. Cd^{2+} ions are too large to enter deep enough into the hexagonal cavities to be fixed close to the OH groups. Some fixation of Cd^{2+} may occur only in the sample heated above 250 °C.

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ELASTIC NETWORK OF LAMELLAR PARTICLES: FORMATION AND RHEOLOGICAL CHARACTERISATION

MAJZIK, A., TOMBÁCZ, E.

Department of Colloid Chemistry, University of Szeged [Kolloidkémiai Tanszék, Szegedi Tudományegyetem], Aradi vértanúk tere 1., Szeged, 6720, Hungary

E-mail: tombacz@chem.u-szeged.hu

In aqueous systems, the colloidal interactions between clay mineral particles are generally governed by local electrostatic field developing around particles due to the neutralisation of surface charges. The composition of aqueous solution influences both the surface charging and the charge neutralisation. Among clay minerals montmorillonite (2:1 layer silicate) as the most often studied swelling clay was chosen for a comprehensive study to show how the pH dependent surface charge heterogeneity of clay lamellae influences the particle interactions in suspensions and the structure of particle network formed in montmorillonite gels. The layers of montmorillonite lamellae have permanent negative charges due to isomorphic substitutions, and pH-dependent charges develop on the surface hydroxyls at the edges. Wyoming montmorillonite sample (SWy–2) was studied. Specific patch-wise charge heterogeneity of montmorillonite lamellae, i.e. oppositely charged surface parts of layers, exists only under acidic conditions. Edge-to-face heterocoagulated structure forms below pH of PZC of edges ($pH_{PZC,edge} \approx 6.5$) and above a threshold salt concentration, where the hidden electric double layer of positively charged edge region has emerged.

In any colloidally stable suspensions the overall particle interaction is repulsive, while more or less loose physical network of adhered particles forms in the unstable suspensions. Whatever the reason, the formation of particle networks strongly affects the mechanical, flow properties of clay suspensions. In general, stable suspensions show liquid-like (viscous) Newtonian flow behaviour with shear thinning or thickening character, while the appearance of plastic character frequently together with thixotropy refers to the network formation of aggregated particles. The rheology of clay suspensions is the subject of tremendous works for several decades, especially because of the wide-ranging practical application. It was supposed that the solid-like gels formed spontaneously from the thin lamellae due to Coulombic attraction between oppositely charged parts of montmorillonite plates have elastic character within a limited range of applied stress, which is presumably comparable with the characteristic yield values of particle networks.

Characteristic changes in gel formation and in rheological properties induced by decreasing pH in dense suspensions containing 0.01 M NaCl provided experimental evidence for the structure of particle network. Static and dynamic methods were used to study the viscoelastic properties of mont-morillonite gels. Several series of creep tests and forced oscillation measurements were performed. A significant increase in thixotropy and yield values, and also the formation of viscoelastic gels below pH ≈ 6.5 verify that attractive interaction exists between oppositely charged parts of lamellar particles in the less concentrated systems. However, solid-like feature with pronounced viscoelasticity, more or less strong network of lamellar particles with large yield values can form in more concentrated montmorillonite suspensions even at higher pHs. It can be stated that different types of elastic network can form from montmorillonite lamellae depending on the pH of aqueous medium containing 0.01 M indifferent electrolyte: a) strong attractive gel with significant elasticity forms in acidic suspensions below the pH of edge PZC (cca. 6.5) due to the electrostatic attraction of oppositely charged edges and faces, b) the formation of attractive gel is probable in neutral suspensions, where no electrostatic attraction exists between neutral edges and negative faces, however, the random collision of lamellae results in edge-to-face particle network with definite elasticity, c) less elastic repulsive gel with rather liquid-like behaviour can form above the pH of edge PZC under alkaline conditions, because the negatively charged edges repel the negative faces of plates, only in more concentrated suspensions. The elastic response of viscoelastic montmorillonite gels is significant, if the applied stress is below or at their yield values, however, above that limits viscous character of suspensions becomes dominant.

Acknowledgements

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INFLUENCE OF THE PREPARATION CONDITIONS ON THE COAGULATION AND ADSORPTION PROPERTIES OF Fe-MONTMORILLONITE

MALIKOV, A. S.,[1] RYAZANTSEV, A. A.,[1] BATOEVA, A. A.[2]

[1] Water Supply Department, Siberian Transport University [Кафедра гидравлики и водоснабжении, Сибирский университет путей сообщения], D. Koval'chuk 191, Novosibirsk, 630049, Russia

[2] Baikal Institute of Nature Management [Байкальский институт природопользования], Sahyanovoy 8, Ulan-Ude, 670047, Russia

E-mail: raastu@irs.ru

Versatile properties of Fe-modified montmorillonite as well as its role in a treatment of sewage are discussed. Especially coagulation and adsorption properties were used for the pollutants removal from various effluents.

The availability of such active centres as ion exchange cations, hydroxyl groups, coordinated non-saturated ions and interlaminar water make clay inviting material in water treatment processes.

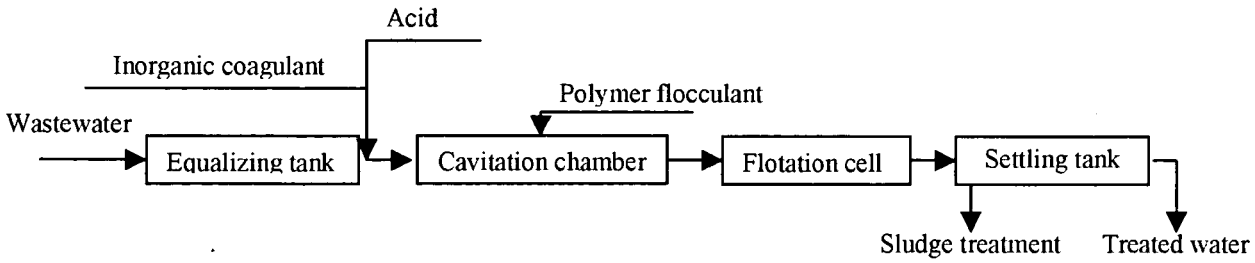
Main task: to develop the recipe for preparation of modified clay able to be scaled up at competitive prices. Refinement and preexchanging of clay have not employed. The activation as well as affinity of montmorillonite to anionic substances was achieved by displacement of ion exchange cations on hydrolysed iron cations using the cavitation bubbles processing of clay in $FeCl_3$ solution. High-speed agitation (3000 rpm) of liquid was employed by a patented device to reduce pressure resulting in hydrodynamic cavitation. The combination of cavitation effect and the shear effect in the chamber causes the clay to reduce to fine particles size of < 60 μm. Moreover the cavitation decomposes water into extremely reactive hydrogen atoms and hydroxyl radicals, which recombine to form hydrogen peroxide and molecular hydrogen. Numerous reduction and oxidation reactions may occur under these conditions.

Coagulation and adsorption properties of Fe-montmorillonite suspension (Fe-MM) were tested during treatment of tanning effluent. The wastewater from this process is characterised by high alkalinity and contains high concentration of both suspended solids (skin, hair-mud) and oil-grease. In addition, chemicals used in this production step, such as lime, soap, ammonia, sulfides and bacteria are discharged with the wastewater.

1st step: the treatment of effluent from liming and unhairing, in which a very high pollution load is generated. About 9 m^3 of wastewater per ton of raw hides are generated, having the following characteristics: chemical oxygen demand (COD) 7,000–35,000 mg/l, pH 12–13, sulfides 1,000–7,000 mg/l. The high content of sulfides in this wastewater is of particular concern. The results indicate on high performance removing of pollutants in COD and S^{2-} values. At dose of Fe-MM 100–120 g/l (clay 10 g/l, Fe^{3+} 0.5–0.7 g/l) the level of contamination is reduced on 80–95%. The similar result was obtained at usage of $FeCl_3$ or mechanical mixture of $FeCl_3$ and clay, however dose of a coagulant in Fe^{3+} values was three-four times more, and the quality of a sedimentation sludge was worse.

2nd step: cavitation air flotation (CAF) process for removal of suspended solids, oils and greases from integrated effluent (liming and unhairing after precipitation of sulfides and COD reduce, fleshing, deliming and bating effluents). This process is based on the formation of a precipitate of the ionic species, using a suitable reagent, and its subsequent removal by attachment to air bubbles to form a flotation scum. CAF device utilises an aerator (rotating disc), which draws ambient air down a shaft and injects micro bubbles directly into the wastewater. The same cavitation cell, as for processing of Fe-montmorillonite, was utilised. It is important to ensure that the coagulant and flocculant must be added at right point and time.

It is necessary to note, that processes of precipitation and flotation generate a voluminous sludge, which has to be taken for further treatment. Since this sludge is not suitable straight on for agricultural purposes the treatment and disposal costs are quite high.



	Raw wastewater	After flotation (cavitation treatment time, min. –4)	
		Coagulant $FeCl_3$ (Fe^{3+} = 0.3 g/l)	Coagulant Fe-MM (Fe^{3+} = 0.3 g/l)
COD, mg/l	7,350	1,650	370

SECONDARY MINERALS IN THE LOWER PERMIAN FILIPOWICE TUFF: A RECORD OF THE LIASSIC HYDROTHERMAL EVENT

MICHALIK, M.,[1] BANAŚ, M.,[2] SMOLAK, W.[1]

[1] Institute of Geological Sciences, Jagiellonian University [Instytut Nauk Geologycznyh, Uniwersytet Jagielloński], Oleandry 2a, Kraków, 30 063, Poland

[2] Institute of Geological Sciences PAS [Instytut Nauk Geologicznyh PAN], Senacka 1, Kraków, 31 002, Poland

E-mail: michalik@geos.ing.uj.edu.pl

The Filipowice tuff formed during Early Permian volcanic activity crops out in the Krzeszowice area (cca. 35 km West from Kraków). Lower Permian sedimentary, volcanic and pyroclastic rocks occur in the Kraków–Upper Silesia Rotliegend basin extended along NE margin of the Upper Silesia Coal Basin. The tuff is a fine-grained pinkish or violet-pinkish porous rock with abundant biotite grains (up to 8 mm in diameter) and lithic clasts of various size and composition (volcanic and sedimentary rocks).

The Filipowice tuff is composed of K-feldspar (with sanidine domination determined using XRD), kaolinite, mica minerals and quartz. In < 0.2 μm fraction the illite–kaolinite ratio is significantly higher than in 0.2–2.0 μm fraction. Illite-smectite minerals are present in both fractions. Apatite microphenocrysts are relatively abundant. K-feldspar in matrix occurs both as anhedral and euhedral rhombohedral crystals (adularia habit). Authigenic hairy illite or illite-smectite occur commonly on surfaces of K-feldspar rhombohedra. K-Ar age determined on illite dominated < 0.2 μm fraction corresponds to the Early Jurassic (199.3[±0.7] Ma). Hematite flake aggregates can also be present on K-feldspar rhombohedra surfaces or partly intergrown with rhombohedra. K-feldspar phenocrysts are strongly kaolinised (kaolinite partly fills voids in phenocrysts). Kaolinite occurs also on rhombohedral K-feldspar, in rock matrix or on biotite. Mafic minerals phenocrysts are partly or completely replaced by Fe- or Fe-Ti-oxides. Secondary barite aggregates are scarce.

Intense K-rich fluids related alteration of the Filipowice tuff is suggested by high K_2O content (8–12wt% according to Kordek and Gruca, 1980; Madeja, 1986), high K_2O–Na_2O ratio (from 10 to 30), and great abundance of authigenic adularia-type K-feldspar. Adularisation of rhyodacite from the Krzeszowice area was described by Słaby (1990). Presence of K-rich volcanic rocks in this area is wide-spread and their metasomatic ("kalification") or primary magmatic origin is discussed by numerous authors (cf. Czerny and Muszyński, 2000 and references cited therein).

Smolak and Michalik (2002) suggested that K-alteration of the Filipowice tuff was related to post-magmatic K-rich fluids or to downward percolation of alkaline marine water from salinary environment developed on elevated areas during Early Muschelkalk (Brniak, 2000). Age determination of illite formed during alteration of tuff indicates that process corresponds to the Early–Middle Jurassic hydrothermal event noted in whole Europe. Hydrothermal activity resulted in diagenetic illite growth in various sedimentary basins in Western and Central Europe (Clauer et al., 1996; Liewig et al., 1987; Michalik, 2001; Zwingmann et al., 1999) and alteration of Late Carboniferous-Early Permian volcanic rocks in Central Europe (Goll et al., 2003; Jacobs and Breitkreutz, 2003; Pękala and Michalik, 2003). The age of alteration of the Filipowice tuff roughly corresponds to the Mesozoic thermal event noted in NE part of the Upper Silesia Coal Basin (160–170 Ma; Środoń et al., 2003)

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ALUMINATED LAYERED SILICATES AS PRECURSORS OF MESOPOROUS MOLECULAR SIEVES

MICHALIK, A.,[1] WŁODARCZYK, W.,[1] LEWANDOWSKA, A.,[1] SERWICKA, E.,[1] GAWEŁ, A.,[2] BAHRANOWSKI, K.[2]

[1] Institute of Catalysis and Surface Chemistry PAS [Instytut Katalizy i Fizykochemii Powierzchni PAN], Niezapominajek 8, Kraków, 30 239, Poland

[2] Faculty of Geology, Geophysics and Environmental Protection, University of Science and Technology [Wydział Geologii, Geofizyki i Ochrony Środowiska, Akademia Górniczo-Hutnicza], al. Mickiewicza 30, Kraków, 30 059, Poland

E-mail: bahr@uci.agh.edu.pl

In 1993 a synthetic procedure describing preparation of the so-called folded sheet mesoporous materials (FSM) from the synthetic mineral kanemite (Inagaki et al., 1993) has been reported. Kanemite is a layered sodium silicate, with formula $NaHSi_2O_5 \cdot 3H_2O$, built of negatively charged tetrahedral silicon oxo-hydroxy zig-zag layers intercalated with positively charged octahedral layers of hydrated sodium cations, which are susceptible to cation exchange. Exchange of sodium cations for the cationic surfactant species results in the rearrangements within the silica layers and formation of structures with honey-comb appearance. Removal of the surfactant template by calcination produces porous materials of unique properties: hexagonal arrangement of uniform pores whose diameter can be controlled within 2–10 nm by changing the templating species, large specific surface area (over 700 m^2/g), and good thermal stability (up to 1100–1200°K).

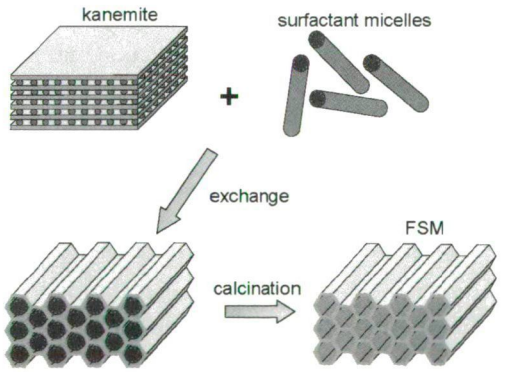

Fig. 1

Purely siliceous mesoporous materials do not contain active sites that would allow for their use as efficient adsorbents, molecular sieves, catalysts, etc. The aim of the present work was to obtain FSM materials substituted isomorphously with aluminium, in order to generate cation exchange properties in the FSM material. The first step of the preparation procedure involved the synthesis of a sodium silicate precursor, which, upon hydration transformed into kanemite. Alumination of the material has been carried out at this stage, by adding $Al(NO_3)_3$ to the synthesis mixture. The XRD patterns of the obtained solids pointed to the presence of several polymorphs of $Na_2Si_2O_5$, whose relative content depended on the amount of Al dopant. Subsequent hydration yielded solids which, beside XRD pattern characteristic of kanemite, showed also reflections assignable to a silicic acid $H_2Si_2O_5$ $7H_2O$. The contribution of the latter increased with the growing amount of Al substitution. A certain amount of amorphous silica, evidenced by a broad envelope centred around d = 0.35 nm, could be found in all solids. Upon treatment with the cationic surfactant (HDTMA, hexadecyltrimethylammonium chloride) and subsequent calcination all materials produced FSM-like structures as demonstrated by the characteristic XRD patterns typical of a hexagonal lattice. The observed d_{001} spacings depended on the Al content and were in the range 3.7–4.2 nm. Solid-state MAS NMR of ^{27}Al showed that in all samples Al occupied tetrahedral positions. Textural properties of the samples were determined from the nitrogen adsorption isotherm at 77°K. The BET specific surface areas were in the range 700–1000 m^2/g. The pore size distribution analysis with BJH method confirmed that all FSM materials were characterised by a uniform pore diameter, ranging from 2.4 nm for FSM without Al and with 2.5at% Al, to 2.8 nm for FSM with 5% Al.

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WEATHERING RATES AND CLAY MINERAL ASSEMBLAGES IN SOILS OF DIFFERENT CHRONOSEQUENCES DEVELOPED ON MARLS AND CALCAREOUS SANDSTONE FLYSCH DEPOSITS IN ISTRIA, CROATIA

MIKO, S.,[1] HASAN, O.,[1] MILEUSNIĆ, M.,[2] PEH, Z.,[1] MESIĆ, S.[1]

[1] Institute of Geology [Institut za geologiju], Sachsova 2, Zagreb, 10000, Croatia
[2] Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb [Rudarsko-geološko-naftni fakultet, Sveučilište u Zagrebu], Pierottijeva 6, Zagreb, 10000, Croatia
E-mail: smiko@igi.hr

Chronosequences of soils developed from Eocene flysch, in two small catchments (Argila and Bazuja rivers) in Istria, were studied with respect to their soil mineralogy and chemistry. The catchments are a part of accumulation-denudation type of morphostructure characterised by rapid denudation processes developed on Eocene flysch deposits. The flysch bedrocks are turbidite deposits of alternating marls and arenites. The calcarenites contain quartz, feldspar, mica grains and lithoclasts of both carbonate and silicate rocks (chert, quartzite and schists). The chronosequences of soils developed on these deposits contain quartz, muscovite and illitic material, calcite in the deeper part of the profiles, feldspars, and the clay minerals dominantly represented by expandable clays (probably smectite) and by small amount of kaolinite. Chemical weathering was evaluated with the aid of bulk chemistry analysis focused on major elements, zirconium and rare earth elements (REE) at 32 sites and the mobility of elements was characterised with the mass transfer coefficient (eluvial–illuvial coefficient, EIC) assuming Zr as the conservative component and the saprolite-rock boundary samples as the least weathered. Due to agricultural land-use practice in the Argila catchment the physical processes significantly contribute to amount fine carbonate-rich rock debris within the soil profiles, which resulted in a mass transfer ≈ 0 or slight accumulation for all major elements and REE in the 0–5 cm horizons and the 5–20 cm horizons. In the same horizons of the forest soils of the Bazuja catchment losses of over 30% of Mg and Ca were determined while Al and K loss ranged from 23 to 28%. The calculated mass loss of REE was 17% in the topsoil horizons 14% in the deeper horizons. Chemical weathering in the soil horizons and weathering rinds of corresponding calcarenite rocks shows enrichment of REE as well as fractionation of REE occurs indicating a higher mobility of light REE than of heavy REE. Changes in long-term weathering rates were evaluated through comparison of molar ratios of major elements in recent stream sediments, overbank sediment profiles in swallow-hole zones and soil profiles. The elemental ratios and REE show that sediments deposited in the floodplain, swallow-hole areas after storm events are mainly derived from less weathered material and plot close to the calcarenite-marl composition. The effect that natural reforestation and abandoning of arable lands has a critical effect on chemical weathering rates in these catchments causing a loss of Ca and Mg from the top 50 cm of the soil profiles and increasing the overall acidification.

THENARDITE-EFFLORESCENCE INDICATING CAUSE OF THE EXCESSIVE FLYSCH EROSION, SLANI POTOK, CROATIA

MILEUSNIĆ, M., SLOVENEC, D., JURAK, V.

Faculty of Mining, Geology and Petroleum Engineering, University of Zagreb [Rudarsko-geološko-naftni fakultet, Sveučilište u Zagrebu], Pierottijeva 6, Zagreb, 10000, Croatia
E-mail: mcovic@rgn.hr

Significant amount of Mid-Eocene flysch is present in the coastal parts of Croatia. In the whole region flysch is subjected to the erosion to lesser or greater extent. However, there is an excessive flysch erosion in Slani potok ("Salt creek") catchment (in the area of Vinodol) which, together with accompanying landslides, covers an area of approx. 3 km^2. At this location, the total site degradation takes place forming terrains of "badlands" type. Slani potok flysch, as also the one from surrounded area without excessive erosion, is represented mainly with calcareous clayey siltstone and calcareous silty claystone and to lesser extent with marls and silty sandstones. There are no significant differences in the mineral content and grain size distribution of clayey siltstone and silty claystone in the whole area of Vinodol. These rocks contain muscovite and illitic material (up to 30wt%), quartz (up to 25wt%), calcite (up to 15wt%), feldspars (up to 10wt%), chlorite, kaolinite and smectite, and in some samples small quantity of pyrite. There is a great amount of small particles. The particle size fraction < 2 μm and fraction 2–4 μm sum up to 45wt% and to 15wt%.

However, the appearance of efflorescent salt crust on flysch in Slani potok during dry period of the year is unique in the area. The mineral content of white salt crust determined by XRD is represented by thenardite (sodium sulphate) and negligible amount of gypsum. The largest thenardite crystallites observed by means of a scanning electron microscope (SEM) have a diameter of 2 μm. Occurrence of this water soluble mineral indicates that some components of flysch encompass sodium, which accelerates desintegration followed by intensive erosion.

A series of physical and chemical tests are carried out in an attempt to verify mentioned assumption. Flysch samples are submitted to physical tests of stability (pinhole test and cyclic dry-wet repeat treatment) indicating high soil erodibility. Determination of soluble salts in flysch pore water was carried out following modified procedure used by the International Soil Reference and Information Centre (Reeuwijk, 2002). Based on criteria established by Sherard et al. (1976), analysed flysch fall in the group of dispersive, i.e. erodible soils. The analysis of stream water for soluble salts was carried out as well. Obtained concentrations of Na^+ and SO_4^{2-} are manyfold of the average contents in running surficial waters.

Illustrated appearance of thenardite is the first finding of this mineral in Croatia.

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NANO AND MICRO PARTICLES ON BENTONITE CLAY

NAGY, N. M., KÓNYA, J.

Isotope Laboratory, University of Debrecen [Izotóp Laboratórium, Debreceni Egyetem], Egyetem tér 1., Debrecen, 4010, Hungary
E-mail: noemi@tigris.klte.hu

Clay minerals are important constituents of the natural environment. By their interfacial reactions they play an important role in several fields, for example in the nutrient cycle of soils, in the environmental protection, or even in the synthetic chemical industry. One of the interfacial reactions of clay minerals is the adsorption and cation exchange of metal ion.

Metal ions can be adsorbed in the interlayer space of some clay minerals (e.g. montmorillonite) and on the pH-dependent charges, silanol and aluminol sites, on the edges of clay minerals. The ratio of the two ways of cation adsorption depends on pH, but about 80–90% of the cation adsorption comes from the neutralisation of the layer charges, so this way of cation adsorption is determining.

The nature of the adsorption is different: in the interlayer space electrostatic forces are important; the ratio of charge and the cation size determine the adsorption ability. Cations in the interlayer space have their hydrate sphere. This process is the so-called outer-sphere complexation. On the edge charges the chemical properties of the metal ions are significant. The cations adsorb on the edge charges by oxygen–cation bonds, without hydrate sphere. This process is called inner-sphere complexation.

Both ways of cation adsorption primarily lead to the uniform distribution of metal ions on atomic scale. However, additional processes can be resulted in the formation of nano and micro particles in the interlayer space as well as on the outer surfaces. Nano and micro particles on clays have been produced by different chemical procedures, but they can be formed under environmental conditions. In this paper the formation of nano and micro particles on clay minerals under environmental conditions are discussed in metal ions—manganese, lead, zinc, and silver ions—and bentonite systems. A really natural micro particle on clay sediment is also shown.

Manganese(II) ions adsorbed in the interlayer space of montmorillonite by cation exchange reactions are spontaneously oxidised to manganese(IV) under atmospheric conditions. Consequently, the properties relating the oxidation state of manganese are different for the fresh and old manganese-bentonite samples. The concentration, distribution of manganese as well as the structure of bentonite, however, do not change. The increase of the positive charge of manganese demands the neutralisation of the extra positive charge by oxide or hydroxide ions originated from the atmosphere, because the negative layer charge of the clay minerals is constant. The presence of a 2D layer of manganese in the interlayer space of montmorillonite is obvious because the montmorillonite has layered structure and manganese ions are introduced into the interlayer space by cation exchange. For this reason the distribution of manganese ions is uniform (as seen by scanning electron microscope, too) and it does not change under oxidation.

These results show that a two-dimensional nano layer is formed in the interlayer space where manganese ion is bonded to the clay layers by two positive charges and to oxides or hydroxides by the other two positive charges.

Lead ions are adsorbed on clays by two processes: by cation exchange in the interlayer space of montmorillonite and by adsorption on the edge sites. Cation exchange leads to the even distribution of the ions, while the adsorption on the edge sites can act as the initial of a heterogeneous nucleation on particle surface followed by a crystal growth. The nano and micro particles (lead enrichments) seen by SEM and AFM can likely be formed on these nuclei. The production of these particles is not expected from thermodynamic properties under conditions of the bulk solution. Similar micro particles are formed on clay sediments under environmental conditions.

Similar micro particles are observed in the case of zinc ion and silver ion. In case of silver-montmorillonite the reduction of silver(I) to metallic silver can also be observed.

As a conclusion we can say that beside the usual ion adsorption reactions, nano and micro particles can also be formed in the interlayer space as well as on the surface of clay minerals. These particles can be two- (2D) or three-dimensional (3D). Two-dimensional nano layer is formed in the interlayer space of montmorillonite by the spontaneous oxidation of manganese ions under atmospheric conditions. Three-dimensional particles are formed on the surfaces of clay minerals initiated by the metal ion (for example lead or zinc ions) adsorption on the deprotonated edge sites. The formation of micro particles on the surface can also be followed by the redox reaction of the metal ion (e.g. reduction of silver ion).

ADSORPTION KINETICS OF STRONTIUM ION IN CARPATHIAN BASIN BENTONITE SAMPLES

NEMES, Z., NAGY, N. M., KÓNYA, J.

Isotope Laboratory, University of Debrecen [Izotóp Laboratórium, Debreceni Egyetem], Egyetem tér 1., Debrecen, 4010, Hungary
E-mail: znemes@dtragon.klte.hu

Radioactive wastes are very complex systems. A very lot of radioactive metal ions are in the radioactive wastes. Therefore, it is important to know the interaction between the geological formations and radioactive metal ions.

The speed of this interaction is determined by adsorption. It would be important and interesting to know the speed of adsorption and steps of adsorption.

In the last years some papers (Cigna et al., 2000; Fuhrmann et al., 2001; Poinssot et al., 1999) dealt with the interactions between radioactive metal ions and the environment, but the papers hardly dealt with adsorption kinetics of strontium (Liu et al., 1995).

One of the main component of radioactive wastes is ^{90}Sr, which has a medium half-life (about 28 years) and high-energy β-radiation. Adsorption kinetics of strontium ion was measured on Carpathian Basin bentonite samples with radioactive tracer method. ^{85}Sr was used for radioactive tracer, because this radioactive isotope is γ-emitter, so the γ-radiation may be measured more exactly than the β-radiation.

Keeping volume of solution quantity of the sample and Sr(II)-ion concentration constant, the reaction time was changed. The adsorption increased with increasing reaction time to a relative equilibrium adsorption yield.

The kinetic data were evaluated by forms of first rate kinetic equation with different term, generally used for adsorption of ions of low concentration. In the case of five samples (Istenmezeje black, Istenmezeje yellow, Egyházaskesző, Mád–Újhegy, Sajóbábony), the adsorption process could be divided into two steps such as film diffusion and particle diffusion. In the case of the other two samples (Kuzmice gel and Mujdeni gel) the adsorption process could be divided into three steps, where the third step is gel diffusion. The presence of higher amounts of cristobalite can explain the gel phase in these two samples. The rate constants of the steps were determined.

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Table 1: Mineral composition of Carpathian Basin samples (XRD analysis by P. Kovács-Pálffy)

	Istenmezeje black	Istenmezeje yellow	Mád–Újhegy	Egyházas-kesző	Sajóbábony	Kuzmice gel	Mujdeni gel
Montmorillonite	54	74	21	89	50	41	42
Illite	–	2	–	–	10	–	–
Rectorite	–	–	10	–	–	–	–
Quartz	4	1	58	–	6	1	–
Cristobalite + opal CT	33	17	–	–	5	54	54
Amorphous	8	5	3	6	20	3	4

Table 2: Kinetic results

k_1 (min^{-1})	1.24	1.64	1.51	2.70	1.83	2.18	2.33
k_2 (min^{-1})	0.08	0.08	0.07	0.27	0.18	0.36	0.38
k_3 (min^{-1})	–	–	–	–	–	0.02	0.06

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MINERALOGICAL AND CRYSTAL CHEMICAL ASPECTS OF METAL ION ADSORPTION ON MONTMORILLONITES

NÉMETH, T.,[1] TÓTH, M.,[1] DÓDONY, I.[2]

[1] Laboratory for Geochemical Research HAS [MTA Geokémiai Kutatólaboratórium], Budaörsi út 45., Budapest, 1112, Hungary
[2] Department of Mineralogy, Eötvös Loránd University [Ásványtani Tanszék, Eötvös Loránd Tudományegyetem], Pázmány Péter sétány 1/c., Budapest, 1117, Hungary
E-mail: ntibi@geochem.hu

The adsorption of copper, zinc, lead, cadmium, cobalt and nickel ions on four montmorillonites SWy–2, Istenmezeje (Hungary), Oraşu Nou and Valea Chioarului (Romania), with slightly different mineralogy, layer charge, cation exchange capacity, chemical composition and morphology was studied by X-ray diffraction (XRD) and analytical transmission electron microscopy (ATEM). The aim of this study was to reveal the effect of individual, intrinsic features of montmorillonites on the metal ion adsorption and their changes in metal ion adsorbed state.

The adsorption capacity of the studied montmorillonite samples is 0.35–0.4 mol/kg for copper, zinc, lead and cadmium and about the half for cobalt and nickel. Basically the metal ion adsorption of the four samples is determined by the layer charge and the cation exchange capacity of the montmorillonite. The amounts of absorbed cadmium, cobalt, lead, and zinc increase with these two crystal chemical parameters. The copper adsorption is independent from the layer charge; nickel adsorption has inverse relationship. When all these ions are present in the solution in 1000 mg/l concentration, the order of selectivity is the following: Cu > Co > Ni > Zn = Pb = Cd.

Based on ATEM studies montmorillonite crystallites contain 0.5–1.0 atomic percentage metal ions that exceeds slightly the interlayer sodium content of the starting montmorillonites. The decreasing sodium content of montmorillonites with increasing metal ion adsorption supports that the adsorption process basically is going on by ion exchange. Moreover other structural ions for example aluminium may be also removed during adsorption. ATEM measurements strengthened the fact that the role of other mineral impurities present in the montmorillonite samples in the adsorption processes—with some exception—have low importance. The amorphous SiO_2—as a common phase associated with montmorillonites—does not take part in adsorption of heavy metals except nickel and cadmium.

If water vapour content is controlled, the basal spacing of metal montmorillonites is influenced by the species and concentration of the metal ion, and the pH. If all the adsorption sites are full with metal ions, the basal spacing of the copper and lead montmorillonites is 12.5 Å indicating one water layer in the interlayer space. In case of zinc, cadmium, cobalt, and nickel montmorillonites the basal spacing is 14–15 Å, i.e. two water layers in the interlayer space.

Based on XRD analysis the domain size of the adsorbed montmorillonite slightly decreased first, than increased remarkably till 20–40 layers with increasing metal ion concentration of the solution. It suggests that at small metal ion concentrations the crystallites disintegrate and at high metal ion concentration they are restructured. The electron diffraction patterns of the studied montmorillonites remain ring-like, therefore the increase in domain size is not followed by the increase of the three-dimensional structural order of the turbostratic structure.

Except cadmium, metal ions reduced the swelling capacity of the montmorillonites upon glycerol solvation especially the ones having low layer charge. Layer charge studies with alkylammonium method proved that metal ion adsorption reduced the layer charge. Some montmorillonite layers with low layer charge and heterogeneous layer charge distribution may loose all their layer charge due to the small sized metal ions entering the 2:1 silicate structure and causing the partial reduction of swelling capacity. Upon 250°C heat treatment copper and nickel enter the hexagonal cavities or the octahedral vacancies of the silicate lattice (Hofmann–Klemen effect). Cd^{2+} ion does not cause reduction of the swelling capacity because it can not enter into the 2:1 silicate lattice due to its large size.

CLAY MINERALS IN LATE PLEISTOCENE-HOLOCENE SEDIMENTS FROM THE LAKE BAIKAL

NOVOTNA, K.,[1] BEZDICKA, P.,[1] GRYGAR, T.,[1] HRADIL, D.,[1] KADLEC, J.,[2] PRUNER, P.[2]

[1] Institute of Inorganic Chemistry AS CR [Ústav anorganické chemie AV ČR], Řež, 250 68, Czech Republic
[2] Institute of Geology AS CR [Geologický ústav AV ČR], Rozvojová 135, Praha, 165 02, Czech Republic
E-mail: katerina.michalova@post.cz

The profiles of the bottom sediments from Academician Ridge in the Lake Baikal are the most reliable continental climatic records of the Late Quaternary, which have become available in the 1990's. Their interpretation has mainly been based on biogenic proxies, diatom and pollen analysis, but only several attempts have been made to read their mineral record. The reason is the polymineral nature of the sediments, containing several classes of clay minerals, unweathered or partly weathered primary minerals from the lake catchment area, and amorphous silica from the diatom frustules. That hardly permits an unequivocal quantitative analysis using conventional tools. However, for any climatic interpretation of the sedimentary records some quantitative values, so called proxies, are required. The proxy must have a definite, implicit or explicit relation to the actual environmental conditions; let it be terrestrial weathering or syn- or post-depositional conditions.

The sedimentary profile VER98–1–13 obtained from GFZ Potsdam was analysed. The profile dating was based on the variations of the palaeointensity of the Earth magnetic field. The part of series covering the last about 200 thousands years was studied; this time span corresponds to the marine isotopic stages from MIS6 to MIS1 (presence).

The mineral assembly of the Lake Baikal sediments contains chlorite-vermiculite-smectite weathering sequence, possibly including interstratified clay minerals, biogenic SiO_2, amorphous expandable clay minerals, amphiboles, feldspars, and quartz as major components (> 1–5%). Separation of clay fraction in this material cannot be recommended because it is not a priori known what size fraction bears the environmental information, e.g. the chlorite weathering sequence can contain members with varying particle size. Conventional techniques of clay mineralogy are not suitable for such multicomponent mixtures, containing more components with variable composition.

For the identification of the clay mineral components we used X-ray powder diffraction in heated support (HT XRD) at temperatures between room temperature and 250°C. HT XRD has not yet been systematically used for identification of expandable clay minerals, and so it was also applied to reference clays and their homoionic forms. This qualitative method was complemented with quantitative analysis of amount and kind of interlayer (exchangeable) cations that seems to be the most reliable proxy-yielding method in the given complex matrix of the sediments. The resulting estimates of content of expandable clay minerals and the ratio between individual interlayer cations were compared to the magnetic susceptibility that have both direct and indirect relations to the actual climate.

Acknowledgements
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SORPTION OF WATER AND AROMATIC COMPOUNDS ON Li-, HDTMA-, TMA-MONTMORILLONITES WITH REDUCED LAYER CHARGE

PÁLKOVÁ, H., MADEJOVÁ, J.

Institute of Inorganic Chemistry SAS [Ústav anorganickej chémie SAV], Dúbravská cesta 9, Bratislava, 84503, Slovakia
E-mail: uachpalk@savba.sk

To determine the influence of the layer charge on sorption properties of Li-, HDTMA- and TMA-montmorillonites, the series with reduced-charge were prepared from Li-exchanged fine fractions of Cheto (SAz–1, USA) and Cressfield (Cress, Australia) bentonites by heating at 100 to 300°C for 24 hours. The exchangeable Li^+ cations in reduced-charge series were replaced with hexadecyltrimethylammonium (HDTMA) or tetramethylammonium (TMA) cations. The adsorptions of two non-polar aromatic compounds biphenyl and naphthalene were studied.

Heat-treatment caused migration of interlayer cations into the previously vacant octahedra and/or ditrigonal cavities of the tetrahedral sheets. The appearance of new bands near 3670 cm^{-1} and 7170 cm^{-1} in the IR spectra of heated Li-SAz–1 and Li-Cress proved the presence of Li(I) in previously vacant octahedra. The d(001) value of cca. 9.7 Å for samples heated at 300°C indicated the collapse of smectitic, i.e. swelling interlayers and the creation of pyrophyllite-like layers.

As revealed XRD patterns, the configuration of $HDTMA^+$ depended on the layer charge of smectites. For unheated HDTMA-SAz–1 and HDTMA-Cress samples the arrangement from pseudotrimolecular to bilayers transition (20.6 or 18.3 Å) was observed. Samples heated above 150°C contained monolayer configuration of $HDTMA^+$ with d-spacing cca. 13.9 Å. The configuration of TMA^+ was different as that of $HDTMA^+$. Small TMA^+ cations form "pillars" which held two adjacent layers apart in constant distance (13.9 Å). Thermogravimetric measurements showed decreasing amount of $HDTMA^+$ and TMA^+ with increasing temperature utilised for the reduced-charge samples preparation. For HDTMA-SAz–1 series the amount of organic cations decreased from 1.05 mmol/g for unheated sample to 0.29 mmol/g for sample heated at 300°C. The IR spectra of HDTMA- and TMA-montmorillonites revealed the correlation of the area of the CH_3 and CH_2 deformation bands with the amount of alkylammonium cations.

Water sorption experiments showed decreasing hydration of Li-SAz–1 and Li-Cress with the layer charge reduction. The water uptake at 100% RH dropped to 15wt% for samples heated at 300°C (Li-Cress, Li-SAz–1). The presence of alkylammonium cations in the interlayers supplied more hydrophobic character to the smectite surface and a sorption of water decreased in order Li > TMA > HDTMA saturated montmorillonites.

The ability of Li-, HDTMA- and TMA-montmorillonites to adsorb biphenyl and naphthalene was studied. The nature of the interlayer cations played an important role in the adsorptive sufficiency of the samples. Only negligible amount of biphenyl and naphthalene were adsorbed onto unheated Li- and TMA-samples. On the other hand, the sorption efficiency of unheated HDTMA-exchanged samples was high, e.g. HDTMA-SAz–1 adsorbed 43 mg/g of biphenyl from water solution in comparison to TMA-SAz–1 or Li-SAz–1 where only 5 mg/g or 6 mg/g, respectively, of biphenyl were adsorbed.

Heat treatment slightly improved the adsorption of aromatic compounds on Li-samples. On the contrary, decrease of adsorption was observed for HDTMA-SAz–1 heated at 300°C (27 mg/g) in comparison with unheated sample. Thus reduction of layer charge and decreasing amount of $HDTMA^+$ caused the lower adsorption of aromatic compounds.

With increasing amount of TMA^+ cations present in interlayers and decreasing layer charge, the sorption ability of TMA-exchanged montmorillonites markedly increased. The highest adsorption of biphenyl and naphthalene was observed for sample TMA-Cress heated at 180°C (49 mg/g).

These results showed that layer charge significantly influences the adsorption of organic compounds on montmorillonites. Considering all studied samples the most effective adsorbents for naphthalene and biphenyl were HDTMA-SAz–1, TMA-Cress heated at 180°C and TMA-Cress heated at 300°C. These samples adsorbed about 80% of organic compounds present in water solutions of biphenyl and naphthalene.

CLAY MINERALS IN THE JURASSIC (TOARCIAN-AALENIAN) EPLÉNY LIMESTONE FORMATION, ÚRKÚT, HUNGARY

PEKKER, P.,[1] WEISZBURG, T. G.,[1] FÖLDVÁRI, M.,[2] POLGÁRI, M.[3]

[1] Department of Mineralogy, Eötvös Loránd University [Eötvös Loránd Tudományegyetem Ásványtani Tanszék], Pázmány Péter sétány 1/c., Budapest, 1117, Hungary
[2] Geological Institute of Hungary [Magyar Állami Földtani Intézet], Stefánia út 14., Budapest, 1143, Hungary
[3] Laboratory for Geochemical Research HAS [MTA Geokémiai Kutatólaboratórium], Budaörsi út 45., Budapest, 1112, Hungary
E-mail: pekker.peter@vipmail.hu

This study focuses on the clay mineral content of the Middle Jurassic Eplény Limestone Formation, which forms the sedimentary cover of the Úrkút Manganese Ore Formation in the Bakony Mountains, Hungary. The Eplény Limestone Formation is constituted by two alternating lithologies, a siliceous and a clayey one, having irregular thicknesses. The clayey type is mostly loosely cemented, green to greyish green, while the siliceous type is a very hard, light grey rock strongly cemented with silica. Preliminary XPD investigations on bulk samples show the following mineral phases in the clayey type: sheet silicates (with 10 and 15 Å 001 reflection), calcite, quartz, dolomite, possibly some feldspar and in some samples opal. The siliceous type contains sheet silicates under detection limit in almost all cases, the mineral constituents are quartz, opal, calcite and sometimes very little amounts of double carbonate.

Based on the results above we selected two samples to characterise the clay content of the clayey lithology. Grain separation was done through crushing and acid treatment (sample U4/98, 5% HCl) or without crushing and leaching in distilled water (sample 121301), followed by wet sieving (to produce a size fraction below 32 μm) and settling in distilled water (to separate the < 2 μm fraction).

The fractions below 2 μm separated this way were investigated through XPD on oriented and ethylene glycol treated samples. Oriented XPD on sample 121301 showed the presence of four sheet silicate phases, with 14.4 Å, 12.8 Å, 10 Å and 7 Å 001 reflections. After the ethylene glycol treatment the 14.4 Å and 12.8 Å reflections shifted to 17 Å, identifying the two phases as smectite and mixed layer illite-smectite, respectively. The 10 Å, non-swelling phase is a mixture of detrital muscovite and illite, the 7 Å phase is kaolinite. The same phases can be observed in sample U4/98 as well.

On the basis of bulk chemical composition sample U6/98, also belonging to the clayey rock type, showed a total of 29–46% sheet silicate content, depending on aluminium substitution in the tetrahedral layer and the distribution of divalent cations among carbonates and sheet silicates.

Thermoanalytical investigation of the same sample (U6/98) revealed 25% illite-muscovite, 6% montmorillonite and 1.5% kaolinite content of the bulk rock.

In comparison with a study on the clay mineralogy of Jurassic carbonate rocks in the Transdanubian Range (Viczián, 1995), only the Toarcian manganese carbonate sequence shows a clay mineral content (significant proportion of smectite) similar to this study. Since the carbonate manganese sequence is the sedimentary base of the Eplény Limestone, a strong genetic connection between the two formations can be assumed. The similarity in clay mineral content and other sedimentological, mineralogical and micropalaeontological characteristics suggest that the two formations represent the same depositional environment. Therefore the only essential difference between the Eplény Limestone Formation and the Úrkút Manganese Ore Formation is the manganese enrichment of the latter. The above considerations suggest that the manganese enrichment appeared only in a certain part of a sedimentary basin, independently from sedimentary processes as reflected by the clay mineral content of rocks.

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INTERCALATION OF MONTMORILLONITE WITH OCTADECYLAMINE UNDER VARIOUS CONDITIONS

PEREZ SANTANO, A.,[1] BELVER, C.,[1] TRUJILLANO, R.,[1] GIL, A.,[2] VICENTE, M. A.[1]

[1] Departamento de Química Inorgánica, Universidad de Salamanca, Patio de Escuelas 1, Salamanca, 37008, Spain
[2] Departamento de Química Aplicada, Universidad de Navarra, Campus Universitario, Pamplona, 31006, Spain
E-mail: mavicente@usal.es

Expansion of phyllosilicates with organocations, mainly alkylammonium cations, has been widely studied. This intercalation, which courses with the exchange of the compensating cations of the clay by these organic cations, transforms the surface of the clay particles from hydrophilic (organophobic) to hydrophobic (organophilic). Swelling with alkylammonium cations having different chain lengths has been reported. Solids thus formed are usually called organo-smectites, their organophilic character allowing applications in different fields, as in the adsorption of organic pollutants.

We report in this communication a systematic study of the intercalation of montmorillonite with octadecylammonium cations under different conditions. Montmorillonite from Tamame (Zamora, Spain) was used as parent material. Octadecylamine, CH_3–$(CH_2)_{17}$–NH_2, was used as precursor of the intercalating cations, being protonated in situ with HCl. Different studies were carried out varying the reaction medium (using water or ethanol, in which the amine is more soluble), the amine–clay ratio (between 0.5–10.0) and the HCl–amine ratio (between 2 and 95). Finally, simultaneous co-intercalation of octadecylammonium and of the inorganic polycation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ was considered.

Solids are successfully intercalated in most of the experiments carried out. When amine–clay ratio was considered, intercalation was observed in the range 1–3; when this ratio is ≤ 1 the clay is not intercalated, probably because of the very small amount of organic molecules, and when this ratio is ≥ 5, an excess of amine, not soluble, was observed. Basal spacings of the intercalated solids are between 17.2 and 36.7 Å. The amount of organic matter incorporated into the solids also varies widely, up to 40wt% C is fixed. The C–N ratio in the solids intercalated is similar to that in octadecylamine molecule. Specific surface area is very low in all the intercalated solids, in most of them between 3–6 m^2/g, because of the total blockage of the clay porosity by the organic molecules. Co-intercalation of octadecylamine and of the inorganic Al_{13} polyoxocation gives rise to intercalated solids with basal spacings between 17–23 Å, also with a high fixation of organic matter and a high blockage of the porosity of the solids.

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EXPERIMENTALLY DETERMINED RELATIONSHIP BETWEEN WAVENUMBER OF νOH STRETCHING VIBRATIONS AND THEIR FIRST OVERTONES FOR CLAYS*

PETIT, S.

HydrASA Laboratoire, Université de Poitiers, 40 av. du Recteur Pineau, Poitiers, 86022, France
E-mail: sabine.petit@hydrasa.univ-poitiers.fr

Historically, the near infrared (NIR) and middle infrared (MIR) fields of research are somewhat distinct from one another. The MIR user is more concerned with functional groups and spectral interpretation than the NIR user who is often more interested in geostatistical applications. Some mineralogical data for clays and clay minerals in the NIR are available (e.g. Hunt and Salisbury, 1970), mainly because field and imaging spectrometers, and hyperspectral remote sensing work exclusively in the NIR (and visible) region.

Recent results of the NIR region for analysing the crystal chemistry of clay minerals have significantly extended the application of this spectroscopy. Indeed, the higher sensitivity to the OH functional group environment of the NIR compared to that of the MIR enables the more effective detection of a) isomorphous substitutions in talcs (Petit et al., 2004) and nontronites (Gates et al., 2002); b) fixed Li in reduced-charge montmorillonites (Madejová et al., 2000); c) Si-OH groups in acid-treated smectites (Pálková et al., 2003). Another utility of NIR region is to recalculate the positions of the OH vibrational bands in MIR as shown by Petit et al. (1999) for the δAlGaOH and δAlCrOH bands in MIR spectra of Ga- and Cr-bearing kaolinites.

The observed bands in the NIR first overtone region are commonly assigned by analogy with the MIR νOH region. However, to interpret spectra, researchers often need a relationship which allows them to calculate the wavenumbers of the first overtone (2νOH) in the NIR from the wavenumbers of the fundamental (νOH) in the MIR and vice versa (e.g. Bishop et al., 2002; Frost et al., 2001).

The aim of this work is to determine a relationship between the wavenumbers of the first OH stretching overtones ($W_{2\nu OH}$) and the wavenumbers of the OH stretching fundamentals ($W_{\nu OH}$) to help to interpret the near infrared spectra of clay minerals. The energy required for the first overtone is twice the fundamental, assuming evenly spaced energy levels. Since the energy is proportional to the wavenumber, the first overtone should appear at twice the wavenumber of the fundamental. However, due to the anharmonic character of vibrations (the energy levels are not equidistant), the first overtone bands appear at wavenumbers less than twice that of the fundamental bands (e.g. Herzberg, 1945), and X the anharmonicity constant is defined by the following relation: $X = W_{2\nu OH} / 2 - W_{\nu OH}$.

To derive the basic correlation between the νOH and 2νOH wavenumbers, the selected samples are talcs because their absorption bands are narrow, with few overlapping peaks if any, and they are sensitive to a variety of octahedral environments. Furthermore, talcs with various chemical compositions can be easily synthesised.

It is shown that the anharmonicity constant X remains almost unchanged for several types of clay samples. Therefore the relation, established from talcs can be used for other clays.

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ADSORPTION OF SOME MONOSACCHARIDES ON PILLARED CLAYS: PRELIMINARY RESULTS

POPOVICI, E.,[1] BURTICA, G.,[1] SINGUREL, GH.,[2] HANU, A. M.[2]

[1] Department of Chemical Engineering, "Politehnica" University [Catedra Inginerie Chimică, Universitatea Politehnica], pta. Victoriei 2, Timişoara, 1900, Romania

[2] Faculty of Chemistry, „Al. I. Cuza" University [Facultatea de Chimie, Universitatea "Alexandru Ioan Cuza"], bd. Carol I 11, Iaşi, 700506, Romania

E-mail: evelinepopovici@yahoo.com

Pillared clays are a special class of microporous materials that can be obtained by interlayering expandable clay minerals with polymeric oxide, as pillars. The Si-PILCs and Al-PILCs have attracted considerable attention in many organic reactions, adsorption processes, and environmental protection. The paper shows the preliminary results of the adsorption behaviour in the monosaccharide-water-pillared bentonite systems. Separation factors, adsorption excess isotherms of monosaccharide-water mixtures, and adsorption equilibrium diagrams show the complex interaction inside of pillaring bentonites.

The bentonite from Valea Chioarului used in our experiment has a complex composition and contains particularly smectite (64%), illite-smectite interstratifications and numerous traces of feldspar and quartz with cation exchange capacity 92 meq/100g bentonite was used clays, a mixture of swelling agent and pillar precursor. The swelling agent is incorporated within the interlayer species of the clay, serving to prop open the layers in such a way as to allow incorporation of the organometallic compound (tetraethylorthosilicate, TEOS) as polymeric oxide precursor. The pillared clay is obtained after calcination at 673°K. The samples were characterised by XRD patterns, FTIR spectra and adsorption isotherms. The D-glucose (Fluka) and D-fructose (Merck) solutions were used. The equilibrium state was checked by measuring the concentration in the interval 8 to 72 hours.

In our experiments because of the adsorption equilibrium between water and clay is determined only by measuring the change of the bulk concentration, the calculated amount of adsorbed saccharide reflects a global isomeric mixture adsorption. The measure of the adsorption of a liquid mixture is the adsorption excess Γ_2^1:

$\Gamma_2^1 = n^0 (x_2^0 - x_2^1)/m$; where: n^0 is the total number of moles in the original solution; $(x_2^0 - x_2^1)$ is the change in the mole fraction of the monosaccharide solution caused by adsorption; m is the mass of the sample (g).

It is evidently that the raw bentonite prefers the adsorption of water, while pillared clays, both the calcined and not calcined samples, adsorb D-fructose preferentially. As a consequence of the limited solubility of the monosaccharides in water only a small portion of the adsorption excess isotherms could be determined.

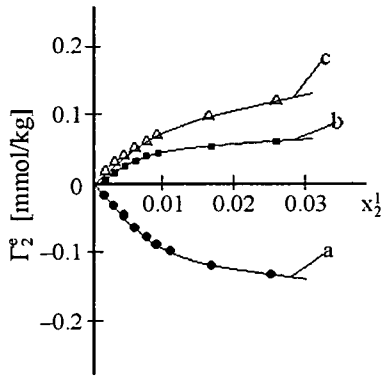

Fig. 1: Adsorption excess isotherms of D-fructose water mixtures on: a) raw bentonite; b) sample not calcined; c) sample calcined.

The obtained data show the ability of the bentonite from Valea Chioarului (Romania), for pillaring processes. The pillaring process was developed the bentonite capacity for monosaccharides separation. Separation factors, adsorption excess isotherms and adsorption equilibrium diagrams show the formation of some strong interaction between monosaccharide and clay surface.

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CONTRIBUTIONS REGARDING SOME RADIOACTIVE ISOTOPES REMOVAL FROM SIMULATED NUCLEAR WASTEWATER USING RAW AND MODIFIED CLAYS

POPOVICI, E.,[1] CREȚESCU, I.,[1] BOTEZATU, E.,[2] HRISTODOR, C. M.,[3] HANU, A. M.[3]

[1] Faculty of Industrial Chemistry, "Gh. Asachi" Technical University" [Facultatea de Chimie Industrială, Universitatea Tehnică "Gh. Asachi"], bd. Mangeron 53a, Iaşi, 700050, Romania

[2] Radiation Hygiene Laboratory, Institute of Public Health [Laborator Igiena Radiației, Institutul de Sănătate Publică], str. V. Babes 14, Iaşi, Romania

[3] Faculty of Chemistry, „Al. I. Cuza" University [Facultatea de Chimie, Universitatea "Alexandru Ioan Cuza"], bd. Carol I 11, Iaşi, 700506, Romania

E-mail: evelinepopovici@yahoo.com

Radioactive waste has a global impact on the environment. The treatment of radioactive liquid waste has as objective both the decontamination process (for its evacuation into environment) and the volume reduction (for its storage or disposal). Treatments by ion exchange are applied on the fluids with low and medium radioactive level and low salts content. Generally, for radioactive effluents decontamination by ion exchange were used the natural and synthetic exchangers with mineral or organic origin. Amoung natural mineral exchangers, clays (kaolinite, montmorillonite, vermiculite, illite) are very used. In this study, the raw and modified clays from Valea Chioarului area (Romania) were used for decontamination of the simulated wastewaters with medium and low radioactivity. The average oxide composition of the raw clay from Valea Chioarului is: SiO_2 69.61%, Al_2O_3 19.7%, Fe_2O_3 1.27%, CaO 0.90%, MgO 2.41%, Na_2O 1.31%, K_2O 0.18%, LOI 5.35% (weight percents). The CEC (cation exchange capacity) value was found 92 meq/100g clay. The specific surface area was about 140 m^2/g. Several single (Fe-clay, Al-clay, V-clay) pillared clays have been prepared by exchange of the charge compensating cations between the clay layers with the larger hydroxications, which are, particularly, oligomeric hydroxy metal cations formed by hydrolyse of metal salts. The oxide pillars, obtained after calcination, sustain the clay sheets and lead to the formation of a bi-dimensional porous network. The specific area of the Fe-pillared clay, and Al-pillared clay was 117 and 280 m^2/g, respectively. The experiments were conducted with solutions that were simulated the liquid radioactive effluents with low medium activity. The water was contaminated with different solutions of radioactive isotopes, which frequently there are in the liquid radioactive overflowing: ^{134}Cs, ^{137}Cs, ^{133}Ba and ^{60}Co. The gamma spectra were analysed taking into account the peak can be ascribed to only one isotope exclusively and a sufficiently high quantum yield, which allows detecting the peak even at low content of an isotope.

The experiments were conducted at ambient temperature and atmospheric pressure, in batch condition, solid–liquid ratio = 1/10 g/ml; pH = 1–2.

The retention of ^{137}Cs on clay samples reached equilibrium in the fallowing order Fe-pillared clay < raw clay < Al-pillared clay. The uptake percentage of ^{137}Cs value tends to increase proportional with increasing surface area of the samples. The uptake percentage of radioisotopes was considerably affected by initial value of solution activity. This experimental finding is related to the diffusion process, knowing that the cationic transit is much faster in diluted solutions.

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ABATEMENT OF PHENOL CONTENT OF WASTEWATERS ON MIXED (Al-Fe) AND (Al-Cu) PILLARED CLAYS

POPOVICI, E.,[1] PODE, R.,[1] HRISTODOR, C. M.,[2] HANU, A. M.[2]

[1] Faculty of Industrial Chemistry, "Gh. Asachi" Technical University" [Facultatea de Chimie Industrială, Universitatea Tehnică "Gh. Asachi"], bd. Mangeron 53a, Iaşi, 700050, Romania

[2] Faculty of Chemistry, „Al. I. Cuza" University [Facultatea de Chimie, Universitatea "Alexandru Ioan Cuza"], bd. Carol I 11, Iaşi, 700506, Romania

E-mail: evelinepopovici@yahoo.com

Generally, the aqueous streams by chemical and related industries contain organic pollutants such as phenolic compounds, which are toxic and poorly biodegradable. In some cases these polluting agents are in very low concentrations, so that the recovery is not economically possible. In other cases, these polluting agents are in very high concentrations so that direct biological treatment is not appropriate. In these cases, it is necessary to use efficient and inexpensive treatments, such as wet peroxide oxidations. In the classical version of this process, Fenton's reagent (Fe^{2+} / Fe^{3+} / H_2O_2) was used.

In this paper the catalytic wet oxidation of phenolic wastewater by hydrogen peroxide (0.1–0.2 mol/l), at room temperature, by mixed (Al-Cu) and (Al-Fe) pillared clays (Al–Cu = 3:1; Al–Fe = 3:1), at pH = 3.5–5.0, was studied. Phenol oxidation was carried out in a thermostated glass batch reactor of 250 ml equipped with a magnetic stirrer, a reflux condenser and a pH electrode. Phenol concentration was determined spectrophotometrically.

This study stress that the studied mixed pillared clay samples exhibit an interesting activity, allowing the total abatement of phenol concentration of wastewaters. Due to its stability and catalytic activity, the mixed Al-Fe and Al-Cu pillared clays could be one of the most promising catalysts.

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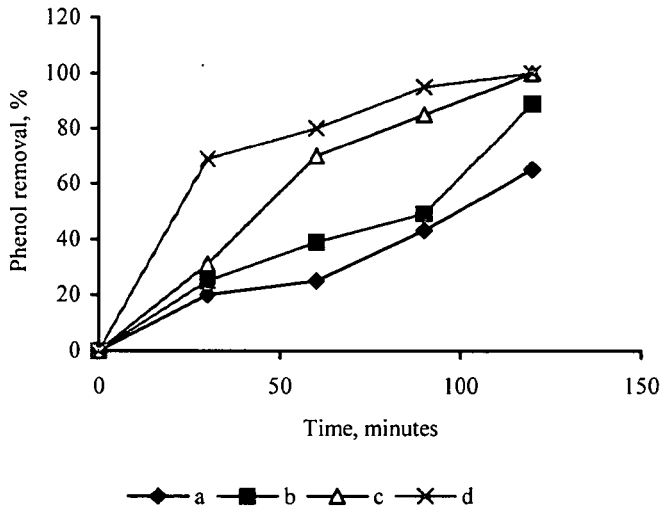

Fig. 1: Phenol removal by different samples:
a) 3Al/Cu PILC, pH = 3.5; b) 3Al/Fe PILC, pH = 3.5;
c) 3Al/Cu PILC, pH = 5.0; d) 3Al/Fe PILC, pH = 5.0

MOLECULAR SIMULATIONS OF MONTMORILLONITE INTERCALATED WITH RHODAMINE B: INTERLAYER AND SURFACE STRUCTURE AND FLUORESCENCE PROPERTIES

POSPÍŠIL, M.,[1] ČAPKOVÁ, P.,[1] MALÝ, P.,[1] WEISSMANNOVÁ, H.,[2] KLIKA, Z.,[2] VALÁŠKOVÁ, M.,[2] WEISS, Z.[2]

[1] Department of Chemical Physics and Optics, Charles University [Katedra chemické fyziky a optiky , Univerzita Karlova], Ke Karlovu 3, Praha, 121 16, Czech Republic

[2] Institute of Materials Chemistry, Technical University of Ostrava [Vysokoškolský ústav chemie materiálů Technická univerzita Ostrava], tř. 17. listopadu 15, Ostrava–Poruba, 708 33, Czech Republic

E-mail: Pospisil@karlov.mff.cuni.cz

Silicates, especially montmorillonites attract attention in wide field of industrial research due to their specific properties. One way of possible montmorillonite modification lies in branch of intercalation processes. Intercalation can be based either on ion exchange (original ion exchange cations are replaced by organic cations) or ion dipole interaction (ion exchange cations remain and organic species are intercalated into interlayer space). Intercalation of optical active species is special and very interesting area because of silicate layers are transparent in visible spectra. The optical active cations (rhodamine B) were intercalated into interlayer space (Pospíšil et al., 2003) and also were remained on the surface of silicate layers. So, the knowledge of structure properties relationship is crucial for describing optical properties of these intercalated samples.

Structure analysis showed that the interlayer and the surface structures are very different in arrangement of rhodamine B cations with respect to silicate layers. Moreover the structure arrangement strongly depends on the guest concentration in the intercalation solution and on the way of sample preparation. The increasing of rhodamine B concentration change arrangement of guest in relative proportions of monomers, dimmers and higher aggregates adsorbed on the external surface and intercalated into the interlayer space. These changes in rhodamine B arrangement can be observed by experimental methods such as X-ray diffraction and fluorescence. For correlation of structure and fluorescence changes molecular mechanics and classical molecular dynamics were used. Molecular simulations were carried out in Cerius^2 modelling environment.

Combination of theoretical and experimental methods show: a) the surface and interlayer structure for given sample is different and b) the concentration dependence of rhodamine B cations arrangement is different for the surface and interlayer structure. The most important difference between surface and interlayer structure occurs in case of fully exchanged samples i.e. between the models with four rhodamine B cations per one 3a×2b×1c supercell in the interlayer space of montmorillonite and four rhodamine B cations per one 6a×2b surface supercell of montmorillonite. In the interlayer space the most stable structure with the highest sublimation energy (calculated by molecular mechanics method) is the bilayer arrangement of rhodamine B cations with xanthenes parallel with the silicate layers. However on the fully exchanged sample surface the most stable structure is the J-dimeric arrangement with xanthene planes tilted to the surface of silicate layer.

Fluorescence measurements of the samples show that increasing loading of rhodamine B cations leads to the red shift of the fluorescence band. However the fluorescence band shape exhibits more complicated behaviour in dependence on concentration. The irregularity in the concentration dependence of these spectral characteristics can be described as a result of joint action of surface and interlayer arrangement of rhodamine B cations in montmorillonite structure.

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POLLUTANT TRANSPORT INVESTIGATED THROUGH AN EXPANSIVE CLAY

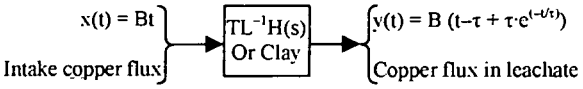
PROUST, C.,[1] LE FORESTIER, L.,[1] JULLIEN, A.,[2] LEDEE, R.,[1] ROBERT, J.-L.[3]

[1] École Polytechniques de l'Université d'Orléans, 8 r. Léonard de Vinci, Orléans, 45072, France
[2] Laboratoire Central des Ponts et Chaussées, r. de Bouaye, BP 4129, Bouguenais, 44341, Francel
[3] Institut des Sciences de la Terre d'Orléans, Université d'Orléans, 1a rue de la Férollerie, Orléans, 45071, France
E-mail: chantal.proust@univ-orleans.fr

In the framework of domestic waste disposals, the in situ compaction of soil is usually used to obtain engineered clay barriers with suitable confining properties. Permeability and pollutant retention are the major properties which should be investigated in this context for barrier evaluation. Considering clay barriers in contact with waste leachates, they may be saturated by solutes of various chemical compositions, including in particular toxic heavy metals. In this context, the expansive Fo-Ca clay, a natural Ca-smectite from the Paris Basin of Ypersian (Sparnacian) age, was chosen because of its very low permeability and ability for pollutant retention through cationic exchanges. The smectic is associated with kaolinite (up to 20%), and minor quartz, calcite, goethite and gypsum.

An experimental work (Jullien et al., 2002) was performed to analyse the Fo-Ca performances when submitted to chemo-hydro-mechanical coupled effects produced by soaking the clay with a polluted solute. For this purpose, tests were performed using 10^{-1} mol/l $Cu(NO_3)_2$ solution. The evolution of leachate chemical composition was carried out as a function of time in order to characterise the ability of the clay to copper retention (Fig. 1).

The previous studied clay samples can be considered as a system submitted to an external parameter (x(t)) and delivering a response to it (y(t)). The copper behaviour can be modelling with a like global equation 1.



where B is $\delta M/\delta t$ (with M is the molar concentration of the input copper solution (mol/l)), TL^{-1} is the Laplace transform, τ is the time constant (hour), and H the gain in the permanent regime.

Simulated curves using different copper concentrations are presented on Fig. 2. To validate this model, an experiment was carried out with a 0.5 mol/l $Cu(NO_3)_2$ solution. The model allows to predict the behaviour of more dilute copper solution representative of waste leachate through a clay barrier.

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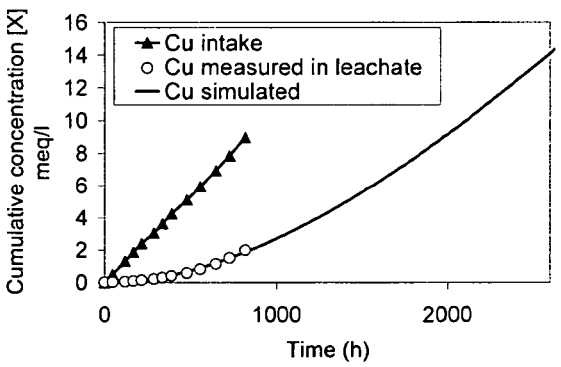

Fig. 1: Experimental concentrations of copper

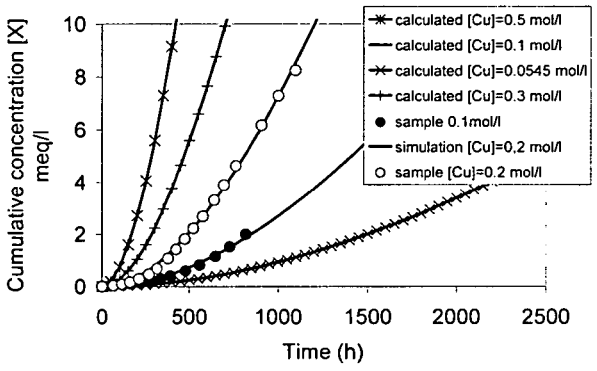

Fig. 2: Simulated curves for different copper concentrations

MINERALOGICAL AND GEOCHEMICAL CHARACTERISTICS OF THE SARMATIAN BENTONITE IN THE BORSOD BASIN (N HUNGARY)

PÜSPÖKI, Z.,[1] KOZÁK, M.,[1] SZÖŐR, GY.,[1] KOVÁCS-PÁLFFY, P.,[2] BARTHA, A.[2]

[1] Department of Mineralogy and Geology, University of Debrecen [Ásvány- és Földtani Tanszék, Debreceni Egyetem], Egyetem tér 1., Debrecen, 4010, Hungary

[2] Geological Institute of Hungary [Magyar Állami Földtani Intézet], Stefánia út 14., Budapest, 1143, Hungary

E-mail: puspokiz@puma.unideb.hu

Because of the frequent rhyolite tuff explosions and the simultaneous eustatic events, the Miocene series of the Pannonian Basin can be regarded as an ideal research object to investigate the eustatic and volcanic control on sedimentary bentonite formation. Among the well preserved transgressive shallow marine bentonite sites of Hungary like Pétervására, Istenmezeje, Salgótarján, Várpalota, Budatétény and Sajóbábony, the latter is recently explored and investigated, where three well identifiable bentonite horizons can be seen separated from each other by placer-like sandy shoreline sediments. Based on the lithological characteristics of the bentonite horizons we could determine three main facies types of bentonites a slightly altered bentonitic tuff, a tuffaceous bentonite with sedimentary feature and a well sorted sedimentary bentonite.

Comparing the X-ray diffraction and thermoanalytical (DTA, DTG, TG) data the montmorillonite concentration calculated by the (110) reflection shows stronger correlation with the TG data than that calculated by (001) reflection. The difference can be caused by the existence of an amorphous phase disturbing the quantitative interpretation of the (001) reflection (diffuse and low intensity). The montmorillonite content determined by thermoanalysis shows strong negative correlation with the amorphous phase of the XRD pattern ($r^2 = 0.62$). These indicate that besides montmorillonite content other important discriminative factor of the facies types is the amount of the amorphous phase.

Based on the investigation of the Hb index (half-width of the 001 reflection), a detailed analysis of the montmorillonite phase was carried out by the comparative interpretation of the whole rock and the fine fraction < 2 μm. The existence of two different montmorillonite types can be proved in the whole rock and in the fine fraction of the bentonitic tuff. The former has much lower, the latter much higher Hb index. In the tuffaceous bentonite the two montmorillonites can be detected only in a few samples while in the case of the sedimentary bentonite the two fractions have the same montmorillonite phase.

The concentration of the amorphous phase in relation to the Al_2O_3 content seems to be important. In this case all of the three facies types can be separated from each other and the strong increasing of the Al content with the decreasing of the amorphous phase can be seen ($r^2 = 0.67$). The appearance of Al^{3+}, Mg^{2+} and Fe^{3+} ions can also be regarded as an important distinctive character. The bentonitic tuff has low Al, Fe and Mg content with an increase of concentrations towards the sedimentary and tuffaceous bentonites. In the case of the sedimentary bentonites the dominance of Fe and Mg ions while in the case of the tuffaceous bentonites the dominance of Al ions can be observed. The strong correlation between Al^{3+} and Fe^{3+} ($r^2 = 0.6$) may refer to their simultaneous incorporation into the octahedral positions in the course of bentonitisation, while the relatively weak correlation between Al^{3+} and Mg^{2+} refers to the less important role of the Mg^{2+}, however, the strong correlation between the Fe^{3+} and Mg^{2+} ($r^2 = 0.73$) proves the simultaneous appearance of the two cations during the alteration. The ratio between Al^{3+} and Si^{4+} in the case of the sedimentary and tuffaceous bentonites approaches the stoichiometric form of the typical montmorillonite.

The rhyolite tuff represents low degree of bentonitisation with a relatively high amount of amorphous phase, the initial alteration of which produced a low concentration of well ordered montmorillonite phase with Na character.

In the case of the tuffaceous bentonite the effect of submarine redeposition caused more intensive alteration of the volcanic glass and thus the strong decreasing of the amorphous phase together with the increasing concentration of montmorillonite. In this case the structure of the forming montmorillonite is less ordered, the dominant cation in the interlayer position is Ca^{2+}.

In the case of the sedimentary bentonite the volcanic glass has a low concentration in the material while the montmorillonite phase is dominant. The structural and geochemical characteristics of the montmorillonite refer to a relatively disordered Ca-montmorillonite with high concentration of Fe^{3+} in the octahedral positions. In this case the substitution of Si by Al leads to the appearance of an Al–Si ratio typical for montmorillonites.

REMOVAL OF THE NON-BIODEGRADABLE DYE ORANGE II BY H_2O_2 OXIDATION ASSISTED BY A Fe(II)/SAPONITE SUPPORTED CATALYST

RAMIREZ, J. H.,[1] MADEIRA, L. M.,[1] COSTA, C. A.,[1] BELVER, C.,[2] VICENTE, M. A.,[2] MARTÍN ARANDA, R. M.,[3] ROJAS, M. L.[3]

[1] Departamento de Engenharia Química, Universidade do Porto, rua Dr. Roberto Frias s/n, Porto, 4200 465, Portugal
[2] Departamento de Química Inorgánica, Universidad de Salamanca, Patio de Escuelas 1, Salamanca, 37008, Spain
[3] Departamento de Química Inorgánica y Química Técnica, Universidad Nacional de Educación a Distancia, Paseo Senda del Rey 9, Madrid, 28040, Spain
E-mail: mavicente@usal.es

Waste streams of textile industry use to be contaminated by non-biodegradable dyes, and removal of such compounds must be done before the streams are returned to the environment. Such removal may be done by oxidation, with or without complete mineralisation, being particularly important the decolourisation achieved. Among several advanced oxidation processes proposed in the literature, the use of the Fenton reagent has proved to be particularly efficient. In this case, the oxidation is carried out with hydrogen peroxide, in the presence of a Fe(II) catalyst. The biggest disadvantage of the homogeneous Fenton process is the formation of sludge containing iron ions, which removal at the end of the wastewater treatment increases the overall costs, besides catalyst loss. To eliminate this drawback, some efforts have been directed to the development of heterogeneous oxidation processes, using supported catalysts.

Supported catalysts are an excellent alternative to bulk catalysts. In them, the active phase is dispersed on the surface of a support, which usually shows large specific surface area, porosity, thermal resistance, etc. Carbons, zeolites, silicas and aluminas are among the most used supports, clays being a good alternative for the preparation of several catalysts.

In the present communication, we report preliminary results on the use of a Fe-clay supported catalyst for the oxidation of Orange II, a non-biodegradable dye. The catalyst was prepared by impregnation of a saponite (Yunclillos deposit, Spain) with Fe(II) acetylacetonate. Previously, the natural saponite had been purified by a conventional dispersion-decantation method, extracting the < 2 μm fraction. Fe(II) acetylacetonate was dissolved in the minimum amount of acetone, and this solution was contacted with the clay, using the "incipient wetness" impregnation method. The precursor amount was that needed for a Fe content in the final catalyst of 5.6%. The solid was then dried at room temperature and submitted to catalytic tests, which were performed in a stirred jacketed batch reactor, being the temperature controlled through a thermostatic bath. The absorbance and the pH were continuously monitored, using a Philips PU8625 UV-VIS spectrophotometer and a pH-meter from EDT instruments RE 357 TX, respectively. For on-line absorbance measurements (at λ_{max} = 486 nm), a continuous flow-through cell was used, within recirculation of the solution with the help of a peristaltic pump.

A 0.2 mM solution of Orange II was considered, being treated with H_2O_2 in presence of the catalyst under different conditions. Temperature (30, 50 and 70°C), initial H_2O_2 concentration (6, 9, 12 and 18 mM) and initial Fe concentration (0.128, 0.18, 0.256 and 0.54 mM), were varied in the different tests (the last two variables allow to control the H_2O_2–Fe ratio), being the pH kept constant at 3.0. The colour of the solution was analysed and it was found that this catalyst is active for removal of Orange II. When increasing the reaction temperature, the time required to achieve colour removal is shorter. The reaction rate also increases with both H_2O_2 and catalyst concentration.

In the best conditions tested, the overall colour removal was above 99% after 280 minutes, but in the first 20 minutes it was already very significant. As changes in colour do not imply necessarily complete oxidation of Orange II, total organic carbon in solution was also analysed. Mineralisation performance seems also to be noteworthy, reaching values above 70%.

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SHORT RANGE ORDER IN PHYLLOSILICATES 2:1

ROBERT, J.-L.

Institut des Sciences de la Terre d'Orléans, Université d'Orléans, 1a rue de la Férollerie, Orléans, 45071, France
E-mail: jlrobert@cnrs-orleans.fr

Ionic distributions are mainly controlled by local charge balance requirements, in all organised compounds. In phyllosilicates 2:1, the charge balance around the OH group, and on the apical oxygens of tetrahedra is a fundamental criterion which manages the cationic distribution in the octahedral layer. Around an OH position, cationic associations can carry 4 (i.e. $2M^{2+}\square$) to 8 charges ($2M^{2+}Ti^{4+}$), and possibly $3M^{3+}$ in non-protonated compounds. In this respect, it is possible to explain why all Li-bearing phyllosilicates 2:1, hectorite, lepidolites, are trioctahedral (exclusion Li-$\square$) and why Li is always in a trioctahedral local environment in mixed tri-dioctahedral solid solutions (Monier and Robert, 1986). Vacant octahedral sites can be either in cis or trans configuration in clays, and systematically trans in micas. Small high-charge cations, generally favour the small octahedron M2 (cis), whereas large cations enter the larger M1 site (trans), but this scheme is rarely completed, and most of structures with differently charged cations, exhibit polycationic sites. The replacement of OH^- by F^- drastically changes the cationic distribution in the octahedral layer, since F^- acts as a point charge, whereas OH^- is a dipole and can share a part of the H^+ charge with the oxygens of adjacent tetrahedra (Robert et al., 1993). This is sufficient to explain the local association between Li and F, as well as Al-F and Ti-F exclusions, for example. Other cases of ordering around an OH group are recognised, as the local association between a protonated apical oxygen of $M^{2+}O_4$ tetrahedron, and an octahedral vacancy. A rare case of $M^{2+}O_4$–$^{[6]}\square$–$M^{2+}O_4$ ordering along c*, is observed in these phyllosilicates. Also interesting is the case of local cationic ordering between tetrahedral and octahedral layer, required to balance charge on apical oxygens of tetrahedra. Local electrostatic considerations lead to conclude that high charge cations in octahedral coordination are associated with Al rather than Si in tetrahedra. So, the well known Al-Tschermak substitution, which involves both tetrahedral and octahedral layers, does not only concerns the whole structural formula, but also the local ordering pattern of Al atoms in adjacent sites.

The distribution of tetrahedrally coordinated cations, Si^{4+} and Al^{3+}, complies first with the Al-Al avoidance rule, i.e. the Loewenstein rule, but a further dispersion of cations is observed, so that the charge distribution is homogeneous (HDC model of Herrero et al., 1989). In other words, the local Si,Al distribution closely follows the bulk tetrahedral layer composition. In high-Al compounds like clintonite, a monosilicic mica, where $^{[4]}$Al–$^{[4]}$Al pairs are dominant, the silicon distribution also shows some ordering, then, this mica does not follow a maximum charge dispersion pattern. On the whole, there is a temperature-dependent equilibrium between the electrostatic energy which favours the cationic dispersion, and the entropic term which favours a disordered distribution (Sanz et al., 2003). Disilicic compounds (Si_2Al_2), like preiswerkite, ephesite, kinoshitalite and margarite should be serious candidates to a perfect Si,Al ordering. But, in these compounds, a minor deviation to stoichiometry is systematically observed, which generates Si-Si associations, for entropy reasons. On the other hand, the structure of these phyllosilicates, deduced from XRD data, are more symmetric than expected, which means the existence of antiphase domains.

In the interlayer space, local ordering of compensating cations are recognised in some cases. In mixed OH-F trioctahedral compounds, divalent cations, e.g. Ba^{2+}, favour those $6TO_4$ rings adjacent to F^-, whereas monovalent cations, e.g. K^+ are preferently associated with OH^-. Small cations, like Li^+, in the anhydrous form, strongly order between two $^{[4]}AlO_4$ tetrahedra of two consecutive layers, for local charge balance requirements.

Dimensional factors also control cationic ordering. This is particularly true with the large cation Mn^{2+} which needs to be associated with a smaller one. This requirement explains the common Al-Mn^{2+} association in manganous phyllosilicates. Another example is offered by the $^{[6]}Mn^{2+}$–$^{[6]}Zn^{2+}$ association in hendricksite, with an average resulting dimension of octahedra similar to that produced by Fe^{2+}–Fe^{2+} pairs.

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GEOTHERMOMETRY ON LOW-TEMPERATURE METAMORPHIC AREAS: PRELIMINARY RESULTS OF CLAY MINERALOGY IN THE BUÇACO SYNCLINE, CENTRAL PORTUGAL

ROCHA, F., GONÇALVES, A. C.

Departamento de Geociências, Universidade Aveiro, Campus Universitário de Santiago, Aveiro, 3810 193, Portugal
E-mail: frocha@geo.ua.pt

Different geothermometers can be used on areas affected by low-temperature metamorphism. Fluid inclusion data, illite or chlorite "crystallinities" and vitrinite reflectance are quite widely used parameters. A scientific program for the assessment of the above mentioned geothermometer data consistency in various Portuguese low grade metamorphic formations has been established and is under development. In Buçaco syncline, Central Portugal, the first results obtained on graptolite remains and fluid inclusions proved a general good agreement of different geothermometric parameters and established some of the general features of the metamorphic framework (Dória et al., 2002).

The main goal of this work is to present recent data concerning clay mineralogy (in particular, illite and chlorite "crystallinities") and to compare these results with those from organic petrology and fluid inclusion study of these metapelitic materials.

In the Central Iberian zone (CIZ) of Portugal, several anticlines and synclines occur in which a Lower Palaeozoic sequence overlays Precambrian-Cambrian metasediments. The Early Ordovician to Early Devonian rocks were affected by very low to low-temperature metamorphism during the Variscan orogeny. The stratigraphical sequence comprises a series of detrital rocks (conglomerates, quartzites, slates and black shales) in a general transgressive sequence. In the Upper Ordovician a volcanic succession of diabases and intrusive dolerites is also present. The Buçaco syncline, in Central Portugal, presents an almost continuous sequence from Lower Ordovician to Silurian. Above an unconformity upper Carboniferous terrestrial sediments also occurs. Several Cretaceous and Quaternary sediments cover part of the syncline.

For the development of the scientific program of testing geothermometer data consistency, a first sampling campaign was carried out in lithologies of different ages in the Buçaco syncline. A total of 30 samples from 5 geological sections (Dornes, Penacova, Poiares, Ceira and Buçaco) were collected. For each sample the mineralogical composition of both total rock and clay fraction (separated by sedimentation, according to Stokes law), was determined by X-ray diffraction (CuKα-radiation) on Philips PW1130/90 and X'Pert PW3040/60 equipments. The clay fraction (< 2 μm) was analysed on oriented aggregates. Qualitative and semi-quantitative mineralogical analyses followed criteria recommended by Schultz (1964), Thorez (1976), Mellinger (1979) and Pevear and Mumpton (1989). Illite "crystallinity" was assessed through the Kübler (1964) index, according to Kisch (1991). Esquevin (1969) index was also assessed.

The results show some consistency with a range of temperatures from 150°C to 200°C in the Lower to Middle Ordovician and of 100°C to 150°C in the upper Ordovician to Silurian. In the near future, the investigation will proceed on the basis of additional sampling for statistical validation of the preliminary results herein presented.

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MORPHOLOGICAL CHARACTERISTICS OF CLAY MINERALS IN DIFFERENT ROCK TYPES OF HUNGARY

SERES-HARTAI, É.

Department of Geology and Mineral Resources, University of Miskolc [Földtan-Teleptani Tanszék, Miskolci Egyetem], Miskolc, 3515, Hungary
E-mail: foldshe@gold.uni-miskolc.hu

Characteristics of clay minerals in different rock types from the Mátra and Bükk Mountains (North Hungary) were studied in order to find some relation between the genesis and morphological features.

The examined samples were divided into the following groups:

- altered andesites and pyroclasts of the Recsk epithermal mineralisation;
- vein-associated altered rocks of the Central Mátra mesothermal mineralisation;
- Mesozoic argillic shales in the Bükk Mountains;
- Oligocene and Miocene argillic sedimentary rocks in the Mátra Mountains;
- Miocene volcano-sediments in the Mátra Mountains.

The clay minerals in the samples were identified by X-ray diffractometry, and thermoanalytical and chemical analysis carried out on separated fractions less than 60 μm in grain size. The morphological characteristics were studied by transmission and scanning electron microscope. The morphological characteristics of clay minerals are as follows.

Almost all examined samples contain illite. The illites of the hydrothermally altered rocks are represented by flawless-edged, lath-shaped crystals with terminal faces. The morphology is shifted towards a squat, hexagonal habit with increasing crystallinity degree. In the sedimentary formations the authigenic illites are elongated, rectangular forms, similar to those in hydrothermally altered volcanics but have no terminal faces.

Kaolinites in the hydrothermally altered volcanics are idiomorphic, platy, pseudohexagonal crystals with usually perfect edges in stacked structures. Occasionally the edges are jagged as a result of post-genetic effects. In the sedimentary rocks the kaolinites are rounded grains or irregular fragments.

Montmorillonite is characterised by the lack of euhedral forms in all rock types. Montmorillonites are most abundant in the halmyrolised pyroclastics. In the Recsk epithermal mineralisation their amount is subordinate but they are more special in the vein-associations of the Central Mátra. The crystals are irregularly shaped, ruggy plates with locally coiled edges.

According to the results, the study of morphological characteristics promotes the solution of genetic questions. However—as clay minerals of different origin can appear in similar forms—the results of other analytical methods and the geological setting also have to be considered.

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TYPOMORPHIC PECULIARITIES OF CAMBRIAN CLAY OF ST. PETERSBURG REGION

SERGEEV, D. S.

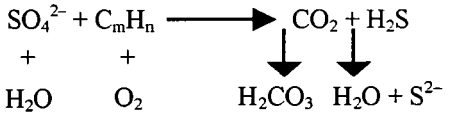
Department of Mineralogy, Saint-Petersburg State University [Кафедра минералогии, Санкт-петербургский государственный университет], nab. Universitetskaya 7–9, Saint-Petersburg, 199178, Russia
E-mail: ds-sergeev@hotmail.ru

The Lower Cambrian "blue" clay of St. Petersburg region is a unique geological object in many aspects. Peculiar interest to these rocks is caused by their slight digenetic transformation taking into account their considerable age (> 500 million years) and their great thickness (cca. 150 m). The region of study is part of the northeast region of Russian Platform. These rocks have big practical importance as building and ceramic materials, otherwise Cambrian clays are regarded to be oil-bearing rocks (deposits in Kaliningrad). In recent times the clays are also studied as very perspective rocks for burial of radioactive waste.

Aim of this work was to make clear the mineral composition of the clays and some features, concerning the clay and sulphide minerals.

The Lower Cambrian clays were divided by a centrifuge into two parts: a pelite and a heavy fraction, which were analysed by X-ray powder diffraction, microprobe and optical observation. The following mineral groups and species were determined: allotigenic minerals are quartz, feldspar, almandine, ilmenite, zircon, kaolinite, chlorite and partially illite; the authigenic minerals are mixed layer mica-smectite, transformed illite, chemical-biogenic pyrite, marcasite, troilite (?) and carbonates. In the pelite fraction interlayer deficient mica of illite series with the polytype $1M_d$ predominates. The changes in symmetry and shape of 001 reflection of mica before and after saturation by glycol indicate increasing smectite contents in mixed layer phase in deeper parts of the section. In the pelite fraction there is also admixture of kaolinite and chlorite. Backwards zone in montmorillonite-illite transformation can be explained by migration of hydrocarbons in sedimentations, which lay up expanded structures and stopped their transformation into illite.

The region studied doesn't include oil deposits. It can be related to its position on the flanks of a syneclise, and resulting shortage of sedimentary and organic matter. Sulphides in the sedimentary basin were formed in several levels of the water-sedimentation regime by bacterial sulphate reduction of dispersed organic matter:



Formation of sulphides in the clays goes on by deepening of the sedimentary basin, where the process of sulphate reduction gives way to the dissociation of H_2S. Otherwise there are also processes of material redeposition, causing enrichment of S^{2-} ions.

The unique feature of the object studied is its weak postsedimentary transformation, which makes possible to observe phenomena, typical for regions with oil and gas deposits: backwards zone in montmorillonite-illite transformation and sulphide mineralisation, such phenomena are normally concentrated in oil-deposit regions.

THE EFFECT OF CLAY MINERALOGY ON RETENTION OF HEAVY METALS BY SOILS

SIPOS, P.,[1] NÉMETH, T.,[1] MOHAI, I.[2]

[1] Laboratory for Geochemical Research HAS [MTA Geokémiai Kutatólaboratórium], Budaörsi út 45., Budapest, 1112, Hungary
[2] Research Laboratory of Material and Environmental Chemistry, Chemical Research Center HAS [Anyag- és Környezetkémiai Kutatólaboratórium, MTA Kémiai Kutatóközpont], Pusztaszeri út 59–67., Budapest, 1525, Hungary
E-mail: sipos@geochem.hu

Adsorption and desorption studies were carried out on brown forest soils characterised by clay illuviation. The samples were taken from the accumulation horizons of soils developed on clayey aleurolites. The clay mineralogy of the studied samples is strongly varying: one of them is characterised by high clay mineral content (45%) and by low charge montmorillonite, while the other one is by low clay mineral content (15%) and vermiculite, as well as chlorite-vermiculite interstratified mineral phases. The Cu, Zn and Pb adsorption experiments were performed in competitive situation, and in the concentration interval of potentially mobile heavy metal fractions of sewage sludge (Cu 200 mg/l, Zn 1200 mg/l, Pb 250 mg/l). The desorption of adsorbed heavy metals from the soil samples was carried out in the following four step according to the sequential extraction after Li et al. (1995): a) exchangeable fraction by $MgCl_2$ extraction, b) specifically adsorbed fraction by NaOAc extraction, c) fraction bound to Fe-Mn-oxides by $NH_2{\cdot}OH{\cdot}HCl$ extraction, and d) fraction bound to organic matter by H_2O_2–HNO_3 extraction.

The affinity of the studied metals to soils decreases as follows, independently of soil composition: Pb > Cu > Zn. Our studies confirmed that the presence of copper and lead has a significant effect on zinc adsorption, while the inverse is not true. The affinity of lead and zinc to soil samples decreases with the dominant clay mineral species in the sequence of vermiculite > montmorillonite, while samples characterised by montmorillonite adsorb more copper than the vermiculite dominated ones. Desorption is also a selective process similarly to adsorption, and the mobility of adsorbed metals increases as follows: Cu < Pb << Zn. The ion exchange is of importance primarily in the samples of high clay mineral content. This process is significant in the case of copper and zinc, as well as of lead in samples characterised by montmorillonite, and vermiculite, respectively. The ion exchange of zinc is more important than the specific adsorption of this metal, because metals characterised by high affinity to soils (Pb, Cu) are adsorbed mainly on the specific sites in competitive situations.

Clay minerals in soils can play an important role in the immobilisation of an eventual heavy metal contamination. The immobilising effect of a soil decreases with the increasing number of polluting metals, and a very small pH change (one unit) can result in loss of an important part of this capacity. The advantage of complex soil composition is that soil acts as a selective buffer for the change of natural conditions. The loss of the buffering capacity of one of the soil compounds does not result in the loss of effect of the other components.

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A CRITICAL REVIEW OF THE ELECTROKINETICS OF CLAY MINERAL PARTICLES

SONDI, I.

Center for Marine and Environmental Research [Zavod za istraživanje mora i okoliša], Ruđer Bošković Institute, Bijenička 54, Zagreb, 10000, Croatia
E-mail: sondi@irb.hr

Chemical properties of soils and aquatic sediments are largely determined by the surface physicochemical interactions at the mineral surface and aqueous interface (Stumm, 1992; Sposito, 1984). Electric charge and ionic interaction of complex surface processes is conveniently studied by electrokinetic measurements (Hunter, 1986; Williams and Williams, 1978; Sondi et. al., 1996; Leroy and Revil, 2004). Its outmost importance is in studies of clay minerals the main components of suspended matter and sediments in natural aquatic systems (Sondi and Pravdić, 2001; Sondi and Pravdić, 2002).

This lecture discusses the electrokinetic properties of clay mineral particles, based on knowledge of diversity of their structural properties, chemical composition, and surface physicochemical interactions. Such studies have been spawning much interest in environmental science and material chemistry studies.

Numerous investigations have shown that organic matter adsorbed at the particle surfaces, modifies the original physicochemical properties of underlying surfaces, and dominates surface interactions of mineral particles with the aquatic medium (O'Melia, 1989; Beckett and Le, 1990; Sondi and Pravdić, 2001). In natural aquatic systems, the omnipresent humic substances are the most important component of the organic film covering the surface of mineral particles, particularly of high adsorptive capacity clay minerals (Sposito, 1984). Therefore, this lecture also describes the influence of adsorption of humic macromolecules on electrokinetic properties. As a real life example, the electrokinetic behaviour of suspended clay mineral particles from the River Raša (Istrian Peninsula, Croatia) will be discussed in view of their colloid stability, coagulation and sedimentation (Sondi et. al., 1995).

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ILLITE-SMECTITE AS A PALAEOGEOTHERMOMETER

ŚRODOŃ, J.

Institute of Geological Sciences PAS [Instytut Nauk Geologicznyh PAN], Senacka 1, Kraków, 31 002, Poland
E-mail: ndsrodon@cyf-kr.edu.pl

Fifty years have passed since Kübler and Weaver first observed that 001 XRD peak of illite changes systematically with depth and ascribed this change to improving "crystallinity" at higher temperatures. In the late sixties the nature of this change was described in terms of layer ratio and ordering in mixed layer illite-smectite and the techniques for measuring this ratio were developed. In 1979 Hoffman and Hower first proposed to use % smectite (%S) in illite-smectite in shales as a palaeogeothermometer. Based on the then available field evidence they suggested that the transition from random to ordered interstratification takes place at about 100°C and from the nearest neighbor to longer range ordering at about 170°C. In the following years some investigators followed this approach but many criticised it, proposing instead various kinetic expressions, relating %S to a number of factors besides temperature (time, chemistry of pore water, type of ordering, chemistry of original smectite).

Despite very abundant literature on the smectite illitisation in shales accumulated since Hower times, its validity for solving this controversy remains limited for two reasons:

- the %S measurement in shales is difficult and the numbers have to be examined critically before using them;
- the burial history of investigated section often is not reported, so only the present-day temperatures and not the maximum palaeotemperatures are available.

The examination of the published data, taking these two aspects into account, makes the present author believe that John Hower was right. Particularly convincing is the evidence of Price and McDowell (1993), who found randomly interstratified clays in Proterozoic shales from the Lake Superior basin, which have never been deeply buried. %S profile of the East Slovak Basin (Šucha et al., 1993) has been used in the following studies to calibrate palaeotemperatures.

Three regional studies of the present author and his coworkers seem to support Hower's palaeogeothermometer and suggest that it is more reliable than widely used organic indices.

1) The Cambrian clays of Estonia, which have never been buried more than 1000 m contain cca. 20%S illite-smectite, and this occurrence was used as an argument in favour of low-temperature time-dependent illitisation. Organic indices support this conclusion. However, K-Ar dating of illite-smectite from Estonian bentonites revealed short-lasting illitisation event, coincident with the Caledonian orogeny (cca. 390–400 Ma).

2) The Carboniferous shales of the Upper Silesia Coal Basin contain R > 0 illite-smectite at the present-day erosional surface, which is inconsistent with R_o data for never deeply buried E part of the basin. K-Ar dating indicates Cretaceous heating event in the E part and the apatite fission track (AFT) dating supports IS against R_o evaluation of the palaeotemperatures (> 125°C).

3) %S in the Oligocene shales of Podhale flysch basin evolve gradually NW to SE from > 60 to < 15%S. 110–120°C palaeotemperature isoline based on %S is coincident with the line of total resetting of the detrital AFT ages (125°C). R_o numbers are erroneous because of overwhelming detrital vitrinite contamination.

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GLAUCONITIC GRAINS IN THE MAGURA BEDS FROM THE POLISH OUTER CARPATHIANS

STARZEC, K.

Institute of Geological Sciences, Jagiellonian University [Instytut Nauk Geologycznyh, Uniwersytet Jagielloński], Oleandry 2a, Kraków, 30 063, Poland

E-mail: star@geos.ing.uj.edu.pl

Oligocene deposits containing glaucony which crop out in the northern part of the Magura Nappe in the Polish Outer Carpathians were investigated from the mineralogical and sedimentological point of view. The upper part of these deposits called the Magura Beds consists of sandstones and shales. They are up to 900 m thick and are considered to be formed by gravity flow processes in weakly oxic environment (Leszczyński and Malata, 2001). Five representatives samples of sandstones were collected from two profiles in Ropica and Folusz villages.

To separate glauconitic grains, the samples were disaggregated and sieved to obtain the size fraction > 0.063 mm. The fraction was then magnetically separated, submitted to acetic acid treatment and ultrasonic cleaning to remove carbonates and any potential contaminants. Finally, non-glauconitic grains were removed by hand-picking under a binocular microscope. The purified glauconitic sample was submitted to further investigations: the morphologic features and internal structure were studied by applying optical microscopy and scanning electron microscopy, the EDS analyses gave a statistical approximation of the chemical composition and basic mineralogical data were obtained using X-ray powder diffraction.

In the studied beds the glaucony occurs only as a granular facies. The green grains are one of the components of the framework in which they constitute up to 10% of the composition. The grain size ranges from 0.06 to 0.5 mm but the fraction < 0.2 mm is predominant. The grains are mainly dark green in colour (light coloured grains represent only a few percentage of each sample). They exhibit mostly three types of morphological forms: spheroidal-ovoidal, tabular-discoidal and irregular, which is characteristic of broken grains. Usually the surface of the grains is smooth and glossy but cracked grains are also frequent. SEM observations revealed random aggregate of flakes within the grains as the only microstructure.

X-ray diffraction analyses show high degree of structural ordering of studied glaucony. Almost all peaks in the diffractograms assigned to evolved and highly evolved glaucony (sensu Odin and Matter, 1981). Some features such as: the positions of first order basal reflection (001), between 10.0–10.3 Å in studied samples, presence of the sharp $(11\bar{2})$ and (112) reflections indicate high degree of glaucony evolution. Nevertheless, absence of the $(11\bar{3})$ and (021) reflections and usually asymmetrical shape of (001) reflection is evidence of small amount of expandable layers in the glaucony structure. The observed d(060) value equals 1.511 Å in three diffraction patterns and 1.512 Å in two others. The chemical composition of the glaucony is as the average reported in the references (Wiewióra and Łącka, 1980), except the SiO_2 content which is higher (51.4–58.3%). The Al_2O_3 content varies from 8.9% to 13.5% and the amount of Fe_2O_3 varies from 15.9% to 23.2%. All samples are characterised by high content of K_2O (> 7% up to 8.6%). Some amounts of MgO, NaO and TiO_2 were also determined.

The chemical composition and X-ray parameters of glaucony samples from both profiles are similar. Only minor differences between these samples were observed. The data indicate that glauconitic grains of each sample reflect the evolved or even highly evolved stages of glauconitisation.

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ACCELERATED DISSOLUTION OF CLAY AND DIATOM BY LAKE BAIKAL BACTERIAL ASSEMBLAGES

ŠTYRIAKOVÁ, I.,[1] LUXOVÁ, M.,[1] ŠTYRIAK, I.[2]

[1] Department of Mineral Biotechnologies, Institute of Geotechnics SAS [Oddelenie minerálnych biotechnológií, Ústav geotechniky SAV], Watsonova 45, Košice, 04353, Slovakia

[2] Institute of Animal Physiology SAS [Ústav fyziológie hospodárskych zvierat SAV], Šoltesovej 4–6, Košice, 04001, Slovakia

E-mail: bacil@saske.sk

Lake Baikal is the world's deepest and most voluminous lake. The sediment thickness reaches a maximum of approximately 8000 m. The attached bacteria were transported by the sedimentation of particles to the less favourable deep cold water of Lake Baikal, where microbial iron reduction is a major respiratory process in low-temperature sedimentary environments.

Temperature appears to be a dominant factor controlling extraction of Fe from clay minerals. The clays are more weathered during the diatom-rich intervals in agreement with warmer climate conditions (Fagel et al., 2002).

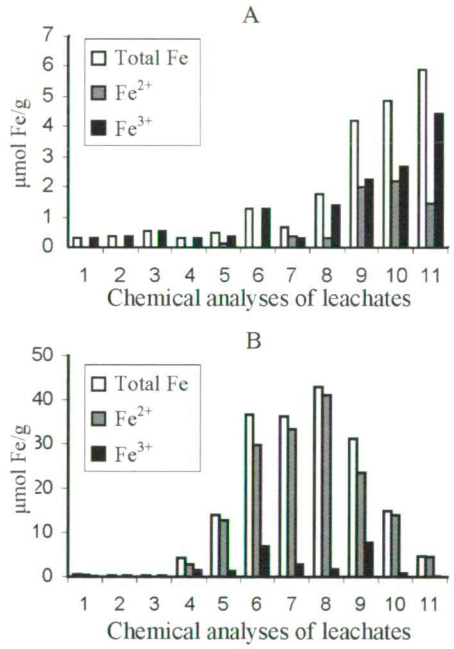

Fig. 1: Release of Fe from clay rich silicate samples during bacterial leaching A) at 4°C and B) at 22°C

The Fe extraction rate is five times lower at 4°C than at 22°C during bacterial leaching of clay (Fig. 1) and diatom rich samples from Lake Baikal. Bacterial activity in Fe reduction from clay rich samples was detected at 4°C later (in 8th leachate sampling) in comparison with cultivation at 22°C when bacterial activity was detected in fourth leachate sampling. The final Fe concentration at 4°C is not known yet because is already monitored. The highest concentration at Fe extraction was 43 µm Fe per gram of clay rich sediment sample and was obtained in 8th leachate sampling. The iron precipitation and formation of Fe mineral phases was observed.

Si extraction from diatom rich samples was also investigated. The silica release after diatom dissolution led to neoformation of clay minerals. It is possible to suggest on the basis of the results of our laboratory experiments how were clay minerals biotransformed during diatom-rich interval period in Lake Baikal.

In oligotrophic waters, microorganisms prefer to live as consortia in biofilms that form at rock–water interfaces (Brown et al., 1999). Lake Baikal is also oligotrophic. That is why it is not surprising that formation of exopolysaccharides in our samples at clay/medium interface, in which Fe was accumulated at 4°C in slime matrix-biofilm, was observed also in our laboratory experiments.

The original iron precipitate in biofilm was mostly in the form of ferrihydrite on the aerobic surface, and of siderite in the anaerobic part of the biofilm (Brown et al., 1999). In case of higher amount of available phosphorus also vivianite could be formed.

These observations confirm the important role of bacteria on biochemical weathering of silicates minerals. It seems that also the parameters such as temperature, formation of organic acids and CO_2 production can influence the biochemical destruction of silicates and bioformation of clay and iron minerals.

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WEATHERING OF ILLITE IN ACIDIC CONDITIONS

ŠUCHA, V.,[1] DUBÍKOVÁ, M.,[1] ŠEVC, J.,[1] CLAUER, N.,[2] KRAUS, I.[1]

[1] Comenius University [Univerzita Komenského], Mlynska dolina, Bratislava, 84215, Slovakia
[2] Centre de Géochimie de la Surface, 1 rue Blessig, Strasbourg, 67084, France
E-mail: sucha@fns.uniba.sk

Two weathering profiles in the Western Carpathians were studied and set of laboratory experiments were conducted to understand stability of illite crystals during weathering process. Both weathering profiles are developed on neogene hydrothermally altered volcanic rocks. First weathering profile represents weathered mixed layered illite-smectites from Dolná Ves deposit with original expandability of 45%. Pure 2M illite from Hodruša with no expandability was exposed to weathering in the second profile.

Natural acidic conditions were created by the organic matter and dissolution of disseminated fine-grain pyrite. The pH of samples was generally in the interval between 3 and 5. Weathering process is in both cases complex and represents parallel dissolution and precipitation of the new mineral phases. In both cases only a small portion of particles was affected by weathering.

A complete dissolution of a certain number of illite particles took place in the case of Dolná Ves illite-smectite weathering. We did not identified any proof for delamination or opening of illite interlayers. Smectite, kaolinite and illite were identified as the new phases present in the upper profile samples. Detrital origin of at least part of the illite was determined by K-Ar dating.

On the contrary number of illite interlayers of limited number of Hodruša hydrothermal illite particles were partly opened to create interstratified illite-smectite in the first phase of weathering. Illite-smectite dissapeared in the second one (upper profile samples). It was most probably replaced by smectite as a result of completed illite opening. K-Ar ages are close to stratigraphic age which means that detrital input of illite can be excluded.

Set of experiments were conducted to show the role of humic acids in the process of weathering. Natural humic acids extracted from the peat were mixed with the powdered Dolná Ves clay. Both separated fine fraction and bulk clay samples were used for the experiment. Clays and humic acids mixed in different proportions were heated at 60° and 80°C up to 42 weeks. Results show slight alteration of illite-smectite and origin of authigenic phases of discrete illite, smectite and kaolinite. Experiment results were almost identical with naturally weathered samples.

AMMONIUM BEARING CLAYS CONNECTED WITH HIGH SULPHIDATION HYDROTHERMAL ACTIVITY FROM CENTRAL SLOVAKIA

ŠUCHA, V.,[1] UHLÍK, P.,[1] MADEJOVÁ, J.,[2] KRAUS, I.,[1] HONTY, M.[1]

[1] Comenius University [Univerzita Komenského], Mlynska dolina, Bratislava, 84215, Slovakia
[2] Institute of Inorganic Chemistry SAS [Ústav anorganickej chémie SAV], Dúbravská cesta 9, Bratislava, 84503, Slovakia
E-mail: sucha@fns.uniba.sk

High sulphidation hydrothermal events are considered to be the first phase of a hydrothermal activity of the Stiavnica stratovolcano situated in Central Slovakia (Western Carpathians). They are connected with base metal stockwork mineralisation, formation of large amounts of secondary quartzite and intensive clay alteration.

Aluminium rich hydrothermal alteration lead to the origin of different clays, mostly: 2M1 illite, pyrophyllite, kaolinite, rectorite and Al-chlorite. Analyses of the clay alteration products show that the high sulphidation fluids were enriched in ammonium. Ammonium was detected in illite and rectorite-like minerals by both FTIR spectroscopy and chemical analysis. Occurrence of ammonium bearing minerals is spread over larger area and it is not concentrated on one spot only. Ammonium is not the dominant cation of the illite interlayers, it occupies in average 10% of the interlayer cation sites. The dominant interlayer cation is potassium. Rectorite from the region has also significant part of sodium in the non-expanding interlayers (up to 35%). Ammonium seems to be a general feature of high sulphidation fluids in the Carpathian Arch. It was reported from similar geological environments in Vihorlat volcanic region (Slovakia) and Harghita volcanic region (Romania).

An interesting feature was observed during XRD analyses of air-dried samples of rectorite. The series of 00l peaks represents a mixture of two sets of reflections. One set can be assigned to rectorites with expandable interlayers with one layer of water molecules and the second set to rectorites with two water layers. Difference disappears when the specimens are saturated with ethylene glycol. During physical separation of the size fractions using centrifuge the particles with two water layers in the interlayer are concentrated in the finer fraction (< 0.2 mm). Particles with one water layer are dominant in the fraction 0.2–2 mm. Clear difference in the water content between two fractions was determined gravimetrically but no difference in chemical composition was found. Different behaviour of two size fractions is regarded as a result of different layer charge connected with the existence of two generations of illite-smectite crystals.

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INVESTIGATION OF HUNGARIAN MONTMORILLONITES AND PREPARATION OF ALUMINA-PILLARED MONTMORILLONITES

SZABÓ, A.,[1] HARTYÁNI, ZS.,[2] NEMECZ, E.[2]

[1] EVM Ltd., Cinkotai u. 26., Budapest, 1172, Hungary

[2] Department of Earth and Environmental Sciences, University of Veszprém [Föld- és Környezettudományi Tanszék, Veszprémi Egyetem], POB 158, Veszprém, 8201, Hungary

E-mail: aszabo@evmrt.hu

Pillared clays (PILCs) are microporous materials. The preparation procedure of pillared clays is based on the intercalation of large metal cations between the clay sheets by an ion exchange procedure. A second step converts these pillar precursors into rigid oxide particles that are tightly bonded to the clay layers.

These inorganic oxide pillared clays offer good properties as ion exchangers and ion selective membranes, protective coatings, and sensors; they can be used in pollutant scavenging and waste management, acid or non-acid catalysed organic reactions.

A variety of pillaring species is known including organic cations, organometal pillars, metal oxide sols, metal complexes, and polyoxycations. Some mixed pillars are used for forming specific active sites in the material. The intercalation of clays with polyoxycations of Al^{3+} resulted in one of the first types of inorganic PILCs. This is also the most investigated pillared layered clay up till now. The main pillaring agent that is responsible for the 10 Å interlayer distance in alumina-pillared clays, is the Al^{3+} oligomer $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$, briefly Al_{13} = Keggin ion. This polyoxycation is the result of a controlled hydrolysis of aluminium salts.

Different kinds of natural samples were taken of the Hungarian bentonite deposits Mád, Koldu and Istenmezeje for preparation and investigation of alumina-pillared interlayered materials. The morphological appearance of Koldu and Mád bentonites is very similar, while Istenmezeje bentonite has a little bit different features: the most jagged, frilled surface of the adhered bunches and the least grain size. For pillaring two different kinds of concentrations of clay suspensions were prepared, namely 10 g/l and 15 g/l.

A pillaring solution of Keggin ion was added to the clay suspensions of raw bentonite and also between the sodium saturated montmorillonites sheets, and after mixing for a few hours the suspensions were filtered and washed. The successfully intercalated montmorillonites with aluminium-polyoxycations were settled to the bottom of beaker, and the sediments looked as a velvet and were softly light. In the intercalated products were detected well discernible colour and textural differences for lower (10 g/l) and higher (15 g/l) concentration clay suspensions. The intercalated materials were air dried at ambient temperature on a glass plate and subsequently calcined at 350°C for 3 hours, and also at 500°C for 2 hours in air.

Resulting alumina-pillared clays were characterised by X-ray diffraction measurements. A basal spacing around 18.5–19.5 Å indicated right away that alumina pillaring occurred since the layer thickness of an anhydrous smectite layer is 9.5 Å and the size of the Al_{13}^{7+} Keggin ion is about 9 Å. The d(001) values of Istenmezeje intercalated montmorillonites were the lowest, the calcined samples had line broadening, as well as the basal peaks of clays were partly returned. Calcined Mád clay samples display the least decrease in d-spacing indicating the best pillared samples for sodium form, both for lower and higher concentrations of clay suspension. Mád and Koldu pillared layer structures absolutely fulfil the minimum criteria of pillared material according to the X-ray. Pillared samples prepared by 15 g/l concentration of clay suspension disclose lower d-spacing loss for all clay than 10 g/l at 500°C temperature. Furthermore, thermal analysis, and BET surface area measurements were applied to examine the new materials. Alumina-pillared Hungarian clay minerals (Na-Mád and Na-Koldu) have specific surface areas around 150–200 m^2/g that nicely meets the accepted requirements. The alumina pillaring was successful in highly concentrated clay suspensions (10 and 15wt%) and highly concentrated aluminium-polyhydroxy complex solutions by simple stirring at room temperature. This method provides an economical way to synthesise alumina-pillared clays in a high scale production.

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ZEOLITE AND CLAY MINERALS AT THE CONTACT OF CRETACEOUS MARLS WITH TERTIARY BASANITE (GRACZE QUARRY, OPOLE, SILESIA, POLAND)

SZELIGA, W.

Institute of Geological Sciences, Jagiellonian University [Instytut Nauk Geologycznyh, Uniwersytet Jagielloński], Oleandry 2a, Kraków, 30 063, Poland

E-mail: szeliga@geos.ing.uj.edu.pl

The contact metamorphism of Cretaceous marls (lower Senonian-Coniacian) (Alexandrowicz and Birkenmajer, 1973) and hydrothermal alteration of tuff in neighbourhood of Tertiary basanites from the Gracze quarry were studied.

Samples collected in the Gracze quarry represent marls and tuff conected with the first stage of volcanic eruptions. According to Kapuściński and Probierz (1999), tuff is composed of pyroxene (augite and diopside), olivine, magnetite, nepheline, clay minerals (illite, montmorillonite) and zeolites (chabasite series). Calcite, serpentine and zeolites replace primary olivine.

Recently the progress of exploitation allowed to collect samples under the basanite. Scanning electron microscope with energy dispersive spectrometry, X-ray diffractometry and optical microscopy were used for the investigations.

The studied tuff is composed of pyroxene (augite-diopside), nepheline, Fe-, Ti-oxide minerals, calcite, serpentine and smectite. Zeolites represent two groups: natrolite type (NAT according to International Zeolite Association classification; Baerlocher et al., 2001) and phillipsite type zeolites (PHI according to this classification). Chemical composition of zeolite minerals is strongly variable, especially in the contents of Fe, K and Mg. Natrolite is present in tuff close to the basanite–marls contact and phillipsite dominates in tuff situated between lava flows. Natrolite occurs in marls close to the cotact; phillipsite is present in samples collected from the lower part of the profile (marls and sandstones beneath marls; Fig. 1). Phillipsite is also present in one sample of marl collected in strongly tectonised zone.

Zeolite minerals occur in spherical forms, grown in the tuff and in lower amount in marls. Spherical forms are also present in cracks in marls. Morphology of zeolite crystals is variable: euhedral prismatic crystals (in tuff and marls) often are overgrown by fibrous branchy zeolite (only in tuff). Almost pure smectite was identified in all tuff samples. In marls I/S mixed layer minerals are present together with mica.

It seems that crystallisation of natrolite and phillipsite was not related separately to temperature or chemical composition of solution, but resulted form overlapping of both of these factors. Probably also other factors were important (e.g. solution–rock ratio controlled by rock permeability). Temperatures determined experimentally (Wirsching, 1979; Wirsching, 1981) for growth of Na zeolites (natrolite) were described by as lower than cca. 150°C (at pH ≈ 12.5 and surplus of Na^+).

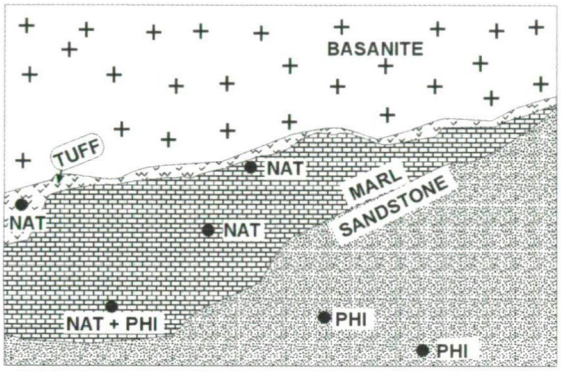

Fig. 1: Sketch of localisation of different zeolite phases (NAT: natrolite, PHI: phillipsite)

Phillipsite crystallises at higher temperature range from 150–250°C (at pH 12–13; Kawano and Tomita, 1997). For growth of phillipsite phase in those temperatures fluids with surplus of K^+ ions are necessary (Wirsching, 1979).

Crystallisation of secondary minerals was related to hydrothermal fluids activity. The sequence: euhedral zeolite → fibrous branchy zeolite → smectite was related to the decreasing temperature. Ions necessary to growth of these minerals were supplied from decomposition of primary minerals in tuff and basanite.

Acknowledgements

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SYNTHESIS, CHARACTERISATION AND CATALYTIC APPLICATION FOR WET PHENOL OXIDATION OF AN IRON-CONTAINING PILLARED CLAY

TIMOFEEVA, M. N.,[1] KHANKHASAEVA, S. TS.,[2] BADMAEVA, S. V.,[3] RYAZANTSEV, A. A.[3]

[1] Boreskov Institute of Catalysis [Институт катализа им. Г. К. Борескова], pr. akademika Lavrent'eva 5, Novosibirsk, 630090, Russia
[2] Baikal Institute of Nature Management [Байкальский институт природопользования], Sahyanovoy 8, Ulan-Ude, 670047, Russia
[3] Water Supply Department, Siberian Transport University [Кафедра гидравлики и водоснабжении, Сибирский университет путей сообщения], D. Koval'chuk 191, Novosibirsk, 630049, Russia
E-mail: timofeeva@catalysis.nsk.su

Microporous solids synthesised by intercalating voluminous metallic complexes between structural layers of swelling clays, such as montmorillonites, are an ongoing subject for research in heterogeneous oxidation catalysis.

High surface area pillared clays (PILC) were prepared from naturally occurring montmorillonites by exchanging interlayer ions with polyoxocations containing a) iron (Fe-PILC), b) aluminium (Al-PILC), c) iron adsorpted onto Al-PILC, and d) iron and aluminium located within the same complex (AlFe-PILC). Polyoxocations $Al_{13-x}Fe_xO_{40}^{7+}$ (x = 0 / 1.5) with like Keggin structure were prepared by base-hydrolysed $AlCl_3$–$FeCl_3$ solutions. The obtained AlFe-PILCs and Fe-PILCs were characterised by far FTIR spectroscopy, ESR, ^{27}Al NMR, scanning electron microscopy and BET surface area measurements.

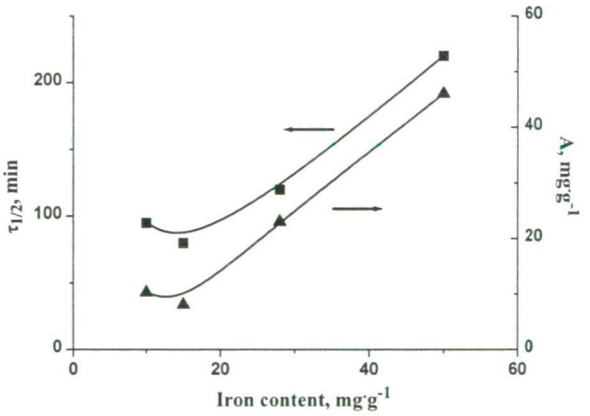

Fig. 1: Influence of the iron content in the Fe-PILCs and leaching of iron from samples on catalyst activity ([PhOH] = 1 mM, $[H_2O_2]$ = 14 mM, [catalyst] = 1 $g \cdot l^{-1}$, pH = 6.2, 50°C)

Catalytic properties of AlFe-PILCs and Fe-PILCs were studied in the wet peroxide oxidation of phenol. It was found that catalytic activities of Fe-PILCs correlated with the iron initially contained in the catalyst and the total amount of dissolved iron by the reaction (Fig. 1).

The induction period which observed on AlFe-PILCs and Fe-PILCs is not produced by diffusion limitations. Probably the induction period account for a) the necessity to reduce ferric into ferrous ions, b) differences in the accessibility to the active sites in the solids and c) differences in the nature of iron in the solids. From ESR characterisation, it was deduced that on Al-PILCs, iron is present as isolated species, probably located on the clay and as oxide clusters, whereas on AlFe-PILCs, an other isolated species was detected, probably located on the pillars. From the catalytic results, it can be concluded that this latter species catalyses more efficiently the total phenol oxidation than the others do.

Important factors affecting catalyst activity and phenol removal efficiencies were studied, i.e. the effect of pH, temperature, catalyst concentration and the stability of the catalyst. It was established that AlFe-PILCs allows a total elimination of phenol without significant leaching of iron ions. It was also observed that by using this catalyst, it is possible to extend the range of pH value (pH = 3.5 – 6.2) for which Fenton-type oxidations can occur. The optimum pH value for AlFe-PILCs is around 3.5–4.0.

The stability of AlFe-PILCs was studied. It was shown that during three cycles AlFe-PILCs can be used without lost catalytic activity and iron leaching.

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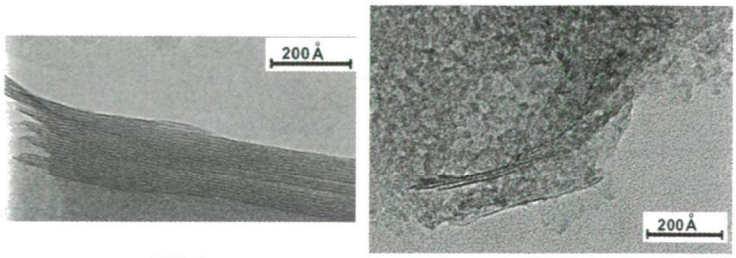


PILC AlFe-PILC (**4**)

Fig. 2: According to SEM data the natural clay are lath-shaped, but air heating AlFe-PILCs have the house of cards structure. In flocculated clays both face-to-face (lamellar) and delaminated (edge-to-face and edge-to-edge) layers occur.

THE INFLUENCE OF CATION INTERCALATING INTO CLAY ON ACIDIC PROPERTIES

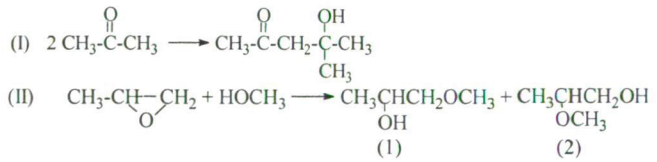
TIMOFEEVA, M. N.,[1] MIKHALIN, N. V.,[2] BUDNEVA, A. A.,[2] KHANKHASAEVA, S. TS.,[2] BADMAEVA, S. V.,[3] RYAZANTSEV, A. A.[3]

[1] Boreskov Institute of Catalysis [Институт катализа им. Г. К. Борескова], pr. akademika Lavrent'eva 5, Novosibirsk, 630090, Russia
[2] Baikal Institute of Nature Management [Байкальский институт природопользования], Sahyanovoy 8, Ulan-Ude, 670047, Russia
[3] Water Supply Department, Siberian Transport University [Кафедра гидравлики и водоснабжении, Сибирский университет путей сообщения], D. Koval'chuk 191, Novosibirsk, 630049, Russia
E-mail: timofeeva@catalysis.nsk.su

Pillared clays (PILC) are applied both as support and active phase in heterogeneous catalysis. These materials may possess acid-base character as well and in some cases they are regarded as super acidic materials. Our task was to find the correlation between the type of cation species (pillaring agent) intercalating into the interlayer space of clay and catalytic activity of PILC ($M^{n+}_{x/n}(Al_{4-x}Mg_x)(Si)_8O_{20}(OH)_4$ montmorillonite type, M = Na^+, H^+, cation of Keggin structure Al_{13}^{7+}). The nature of pillaring agent determine the surface area and pore size. X-ray and BET data show that texture characteristics depends on thermal treatment of Al_{13}^{7+}-PILC.

Acidities of PILCs (Na^+-PILC, H^+-PILC and Al_{13}^{7+}-PILC) were studied by IR spectroscopy both analysing the band due to OH-vibrations and following the adsorption of carbon oxide. Acid strength distribution of the PILC pretreated under different conditions was determined by using an indicator method. It was found that the total acidity was increased in the order: Na^+-PILC > H^+-PILC > Al_{13}^{7+}-PILC (Table 1). The number of acid sites decreases exponentially. As the pretreatment temperature of PILC is increased, the measured number of most strongly acidic sites ($H_0 = -5.6$) increases up approximately 500°C, apparently due to the elimination of water molecules previously guarding the proton.

The catalytic property was studied in the reactions such as the acetone dimerisation (I) and the reaction of propylene oxide with methanol (II):



It was shown, that in both reactions catalytic activity of PILCs correlated with the amount and nature of the acidic sites and increased in the order: Na^+-PILC > H^+-PILC > Al_{13}^{7+}-PILC. In the reaction (II) the selectivity is virtually independent of the nature of the pillaring agent. Catalytic activity increased with increasing total acidity. It was established that catalytic activity depends on pretreatment procedure, namely temperature, nature and ratio pillaring agent–clay. The mechanisms of reactions (I) and (II) in the presence of PILCs was discussed. H^+-MM and Al_{13}^{7+}-MM were more efficient than H-ZSM–5 and bentonite in both reactions.

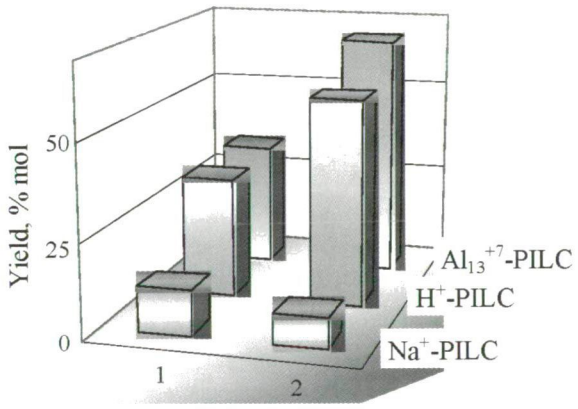


Fig. 1: The reaction propylene oxide with methanol (C_3H_7O / MeOH = 1/10 mol) in the presence of PILCs (3wt%) at 60°C for 6 hours

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Table 1: The main characteristics of PILC

PILCs	d_{001} Å	(A) $k \cdot 10^4$ s^{-1}	(B) Acidity, mmol·g^{-1}	(C) Acidity, mmol·g^{-1}			
				Ho = –5.6	Ho = –3.0	Ho = +3.3	Ho = +4.8
Na^+-PILC	15	2.1	0.03	0.01	0.04	0.30	0.42
H^+-PILC	15	4.7	0.04	0.10	0.20	0.28	0.41
Al_{13}^{7+}-PILC	17	9.3	0.06	0.10	0.24	0.32	0.43

(A) Reaction rate constant of acetone dimerisation reaction (50°C, catalyst 10wt%, PILCs heated at 500°C, 3 hours); (B) Total acidity measured by adsorption CO; (C) Acid strength distribution was determined by Hammet acidity titration with n-butylamine

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SURFACE CHARGE HETEROGENEITY EXPRESSION IN AGGREGATION OF MONTMORILLONITE LAMELLAE

TOMBÁCZ, E.

Department of Colloid Chemistry, University of Szeged [Kolloidkémiai Tanszék, Szegedi Tudományegyetem], Aradi vértanúk tere 1., Szeged, 6720, Hungary
E-mail: tombacz@chem.u-szeged.hu

Montmorillonite layers have permanent negative charges due to isomorphic substitutions, and pH-dependent charges develop on the surface hydroxyls (Si-OH, Al-OH) at edges. Acid-base titration of well defined Na-montmorillonite suspension at different ionic strengths has been proved to be acceptable to characterise the pH-dependent charge development on amphoteric edge sites and to determine the point of zero charge (PZC) of edges. The evaluation of reversible net proton surface excess vs. pH functions has revealed that the OH groups at edges having PZC at pH ≈ 6.5 are less basic than the Al-OH sites of alumina and less acidic than the Si-OH groups on silica surface. Positive charges can develop in a protonation reaction of Al-OH sites at edges only at pHs below cca. 6.5, and deprotonation of Si-OH, then that of the Al-OH sites takes place with increasing pH of solution resulting in negative charges at edges. Therefore, the patch-wise charge heterogeneity of montmorillonite, i.e. oppositely charged surface parts of platelets, exists only under acidic conditions, which may remain hidden at low salt content due to the spillover of the negative electrostatic field emanating from the face of montmorillonite plates. The effect of pH and indifferent electrolytes is mutual; none of them can be interpreted alone.

Coagulation kinetics measurements resulted in reliable stability ratio data for fine montmorillonite sols at different pHs, and provided indisputable characterisation of hetero- and homocoagulation. Edge-to-face heterocoagulation occurs above NaCl concentration 25–26 mmol/l at pH ≈ 4, where the hidden electric double layer (EDL) of positively charged edge region has emerged. Edge-to-face attraction between the poorly charged edges and negatively charged faces of platelets around the pH of PZC of edges ($pH_{PZC,edge} \approx 6.5$) in relatively low concentration of the indifferent electrolytes (typically around 50 mmol/l NaCl) is probable. The homocoagulation of uniformly charged lamellae at pH 8–8.5, formation of face-to-face aggregates requires much higher salt concentration (typically around 100 mmol/l NaCl) to compress the dominant edl on the highly charged faces of particles.

The surface charge heterogeneity of highly anisometric montmorillonite plates influences the ordering of lamellae in the self-oriented films. X-ray diffraction patterns of montmorillonite films prepared from slightly acidic suspensions proved that formation of well ordered layer packages is hindered by the attraction between edges and faces. Random edge-to-face fractal aggregates form below pH ≈ 7, while well oriented face-to-face structure can develop, if the pH of initial suspension is above pH ≈ 8.

Characteristic changes in gel formation and in rheological properties induced by decreasing pH in dense suspensions containing 0.01 M NaCl provided experimental evidence for the structure of particle network. A significant increase in thixotropy and yield values, and also the formation of viscoelastic gels only at and below pH ≈ 6.5 verify that attractive interaction exists between oppositely charged parts of lamellar particles. The lower the pH the larger the amount of positive charges on the edges of montmorillonite lamellae, therefore the attraction between the positively charged edges and negative basal plates becomes stronger with decreasing pH above the critical pH ≈ 4 of the acidic dissolution of crystal lattice.

Acknowledgements

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SUBSTITUTION PROCESSES DURING GLAUCONITISATION

TÓTH, E., WEISZBURG, T. G.
Department of Mineralogy, Eötvös Loránd University [Eötvös Loránd Tudományegyetem Ásványtani Tanszék], Pázmány Péter sétány 1/C, H-1117 Budapest, Hungary
E-mail: zsike@abyss.elte.hu

By differentiating between glauconitic grains of different evolutionary stages within the same population we may get a deeper insight into the glauconitisation process. Previous studies dealt mainly with the highly evolved glauconitic grains (density around 2.8 g/cm^3), which, due to the late evolutionary stage, often camouflaged the steps of glauconitisation.

By studying also the low-density glauconitic grains (starting from ≥2.83 g/cm^3 down to ≤2.33 g/cm^3 with density steps of 0.05 g/cm^3) the glauconitisation process (see also Weiszburg and Tóth, 2004) can be traced back to the starting material. For this purpose, glauconite populations from sandstones of the Upper Oligocene Eger Formation (Hungary) have been studied in detail. The substrates for glauconitisation were volcanic debris (tuff fragments) and biogenic grains (foraminifera tests and test fragments, echinoderm test fragments, snails and faecal pellets). Selected grains have been studied by scanning electron microscopy (SEM equipped with energy dispersive spectrometer) and electron probe microanalysis (EPMA).

The first step of glauconite formation is the primary precipitation of an iron-rich dioctahedral layer silicate of a layer charge around 0.5–0.6 that still contains relatively high amounts of Al (up to 10–12 wt% Al_2O_3). We suppose that volcanic material contribution (e.g. tuff, volcanic debris) plays an important role in the formation of that iron-rich smectite precursor. Two major processes yield these smectites: (1) primary precipitation in semi-confined voids, e.g. foraminifera chambers and other fossil casts, voids of echinoderm test fragments, pores of volcanic tuff/glass and (2) primary precipitation as substitution of the carbonate test material, the (often glassy) matrix of volcanic debris and the chemically less resistant mineral grains within the hosting rock fragments (pseudomorph formation). Smectitic material precipitating in voids is porous at the beginning, and often contains detrital grains up to a size of 40 μm. Smectite formed by substitution is, on the other hand, more compact, of low porosity, and usually does not contain detrital grains. In the case of the carbonate test material substitution, the process seems to progress from the inside, from the already smectitic test-filling material towards the outer surface of the carbonate test.

The main mass of nascent glauconite (i.e. iron-rich smectite precursor) is produced by primary precipitation in voids and substitution of the matrix of volcanic debris. Larger mineral inclusions (up to few tens of micrometres) within glauconitic grains may survive long: unaltered micas and feldspars have been observed to approx. 2.53 g/cm^3 density. A great part of detrital grain inclusions, however, slowly undergoes substitution: this process has been observed at feldspars, chain and layer silicates. The rest of the detrital grains (more resistant minerals like quartz or TiO_2 polymorphs) are supposed to get expelled from the glauconitic grains during the glauconitisation process. Detrital grains are already rare above 2.58 g/cm^3 density. It should be noted that beside chemical resistance, crystal size is of primary importance in determining whether a mineral undergoes glauconitisation or not: unaltered amphibole, muscovite and feldspar crystals are present in the sandstone from the lowest studied grain size fraction on (63–125 μm; feldspar is present even in the clay fraction). This size effect might be coupled by the fact that crystals already in the size range of the glauconite grains can hardly get into a semi-confined environment that favours glauconitisation.

The second phase of glauconitisation is a chemical evolution (for details see also Weiszburg and Tóth, 2004) affecting the void-filling and substituting smectitic materials similarly, so in the final stage there is no real difference between the two initial types. The iron-rich dioctahedral (octahedral occupancy 2.1–2.2) smectite precursor becomes denser and gradually turns into an iron-rich clear dioctahedral (octahedral occupancy around 2.0) mica. This well-known process involves the incorporation of K and Fe (both Fe^{2+} and Fe^{3+}) into the structure parallel to the release of Al.

The described processes result in homogeneous, low-porosity grains at the end of glauconitisation, sometimes even the substrate type is difficult to recognise.

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ANKARA CLAY: ITS GEOLOGY, MINERALOGY, PROPERTIES AND APPLICATION

TURKMENOGLU, A. G,

Department of Geological Engineering, Middle East Technical University [Jeoloji Mühendisliği Bölümü, Orta Doğu Teknik Üniversitesi], Ankara, 06531, Turkey

E-mail: asumant@metu.edu.tr

Upper Miocene-Pliocene continental clastic rocks show a wide-spread distribution in Ankara region. They are well exposed in a number of diverse sized depressions which are separated by a series of highlands. Ankara Basin is an approximately ENE-WSW trending, 18–20 km long and 6–8 km wide depression. It is sedimentary fill, the Yalincak Formation, from bottom to top, consists of three lithofacies as debris flow conglomerate, braidplain conglomerates to sandstones and flood plain finer clastics. They were underlined unconformably by the Triassic graywacke-shale with carbonate blocks, Liassic clastics, Upper Jurassic-Lower Cretaceous limestones, Upper Miocene-Lower Pliocene volcanics and fluvial-lacustrine sedimentary rocks (Kocygit and Turkmenoglu, 1991).

The flood plain finer clastics of the Late Pliocene age Yalincak Formation were referred as "Ankara Clay" which consists of stiff and fissured reddish brown mudstone characterised by caliche nodules and black patches of manganese oxide. The reddish colour (2,5 YR Munsell colour) is due to due high pigmenting colour of hematite and maghemite. This level is dominated by laminations, lensoidal channel conglomerates and normal to reverse type of growth faults. These are the evidences of unstable fluvial setting, climate with seasonal rains and pedogenic episodes interrupting frequently sedimentation of the Ankara Basin. A toposequential relationship is indicated between the palaeosols (relict Red Mediterranean soils) and Ankara Clay based on the erosive conditions and topography in the Late Pliocene period (Mermut, 1976; Cangir and Kapur, 1983). The red colour is related to oxidising conditions and periodic wetting and drying. The red pigment is primarily hematite which was produced by dehydration process during periods of extended subaerial exposure.

The dominant clay minerals in Ankara Clay are discrete illite, smectite, kaolinite, chlorite, mixed layer illite-smectite and mixed layer chlorite-smectite. Kaolinite is also present in small quantities. The degree of crystallinity of clay minerals is poor as revealed by XRD and FTIR data (Aras, 1991). Clay flakes are simply and tightly consolidated and the compaction process cause parallel orientation of them. The non-clay minerals are zoned plagioclase, calcite, quartz, maghemite, hematite, goethite and ilmenite. The coarse fraction of mudstone is derived from graywacke, limestone, andesite, quartzite and schist. Illite and chlorite were originated from schist, phyllite and graywacke while young andesitic volcanics supplied smectite into the depositional basin. The mixed layer clay minerals are the weathering products in an oxidative environment (Aras, 1991; Saglam et al., 2003). Chemically, the bulk samples of Ankara Clay contains 64–57% SiO_2, 11–19% Al_2O_3, 6–8% total Fe_2O, 2–6% MgO, 1–3% CaO, 0.4–1% Na_2O and 2–4% K_2O. The clay fraction, on the other hand, comprise 10–12% total iron as shown by Saglam (2002). This indicate that iron-rich smectite, illite and chlorite and amorphous Fe-oxides dominates the clay fraction.

Extensive studies has been conducted by engineers on the geotechnical properties of Ankara Clay since the majority of the rapid growing Ankara city is sitting on this unit and its expansive character causes important damage on light buildings, road pavements and other engineering structures (Ordemir et al., 1977; Kasapoglu, 1982; Teoman et al, 2003). These properties are treated with special emphasis on its expansive properties which cause important damage on the engineering structures due to swelling, slope instabilities, settlement and landslides. Data collected for geotechnical engineering applications mainly involves mineralogy, grain size distribution, unit weight, specific gravity, compressibility, shear strength, Atterberg limits and index values (liquid limit, plastic limit, plasticity index), moisture content and cation exchange capacity. Works carried out for this purpose indicate highly plastic and expansive character of Ankara Clay. Therefore, research on the stabilisation of the clay material became a necessity.

Due to rapid growth in population, Ankara city faces a yet unsolved environmental pollution problem caused by the disposal of the huge volumes of municipal waste. Widespread occurrence of Ankara Clay makes it a potential material to be used as a landfill liner. Some investigations (Sezer et al., 2003) treated Ankara Clay with special emphasis on its sorption capacity and hydraulic conductivity characteristics in addition to the clay mineralogical composition. The studies show that Ankara clay can be effectively utilised as a component of barrier design in sanitary landfills because of the suitability of its above characteristics.

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THE STUDY OF CLAY PRODUCTS FROM WEAVING WORKSHOP OF KALENDERBER CULTURE (800–600 YEARS B.C.) IN NOVÉ KOŠARISKÁ (SLOVAKIA)

UHLÍK, P.,[1] GREGOR, M.,[2] ČAMBAL, R.[3]

[1] Department of Geology of Mineral Deposits, Comenius University [Katedra ložiskovej geológie, Univerzita Komenského], Mlynska dolina G, Bratislava, 84215, Slovakia
[2] Geological Institute, Comenius University [Geologický ústav, Univerzita Komenského], Mlynska dolina G, Bratislava, 842 15, Slovakia
[3] Archaeological Museum SNM [Archeologicke muzeum SNM], Žižkova 12, Bratislava, 81436, Slovakia
E-mail: uhlik@fns.uniba.sk

Investigation of ancient ceramics provides a field for application of basic mineralogical and petrological techniques. The mineralogical changes during firing of the paste are very useful for an estimation of the ancient firing temperature and firing atmosphere, the nature of the raw material and the technology of the processing. Description of temper can be useful for identification of local or foreign production. Cooperation with archaeologists is also very important. The following contribution had an effort to use and accept of all mentioned aspects at the study of Kalenderber ceramics from Nové Košariská (Dunajská Lužná).

Kalenderber Culture is part of East Hallstadt cultures of the Earlier Iron Age (800–600 years B.C.). Dunajská Lužná belongs to the most important habitant in Middle Europe within the framework of Earlier Iron Age owing to presence and investigation of tumulus. Weaving workshop was discovered during last archaeological research in this area. There was a lot of resident ceramic materials with typical shape and decoration and predominately 170 pyramid weight from 2 looms.

Sherd material is divided to coarse- and fine-wall ceramic according to macroscopic observations. The temper is visible in both type but in coarse-wall sherds can be observed large clasts over 1.5 cm in diameter. However both type belong to coarse ceramics conforming with modified Werthworth granulometric classification (Ionescu and Ghergari, 2002). Size distribution of grains and clasts is bimodal. It refers to purposeful addition the temper into original raw material. There are quartz, feldspar, muscovite and biotite as major minerals of one part of the temper in ceramic. The other type of the temper are lithoclasts. Quartzites predominate over granitic and metamorphic lithoclasts. Ceramoclasts and soil nodules are presented rarely.

The fabric of coarse-wall ceramics has random arrangement. The structure of fine-wall sherds is also chaotic but slight orientation in the outer parts of the sherds was sometimes observed. Very weak features of circular arrangement were noticed in both types of ceramics. Forming and shaping of vessels was probably done by presing them out from a ball of clay by hand and/or beating the clay with use the paddle-and-anvil technique (Shepard, 1976).

Mineralogical composition and structure of matrix suggest a fire temperature about 700–850°C. Ceramics have been fired in reduce or mixed atmosphere with exception of ceramics directly from object. They have been fired for the second time in oxidised atmosphere (workshop was destroyed by fire) and their colour is red.

Wieving weights are different from ceramic materials. They were made from sand-clay material without large clasts and tempers. Weights can be determine as carbonatic for presence of calcite and dolomite. Their thermal adjustment was not higher than 200–250°C because the presence of expanded clay mineral (mixed layered illite-smectite) were observed.

The source of added the temper is from surrounding fluvial sediments of river Danube. The provenance of basic clay material used for production of ceramics is questionable but we suppose local origin. The provenance of raw material used for weaving weights is from local loess.

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THE APPLICATION OF ZEOLITE AND ALGINITE FROM SLOVAKIA FOR ZEOPONIC SUBSTRATES

UHLÍK, P., VAJDOVÁ, M., SHIWA, A.

Department of Geology of Mineral Deposits, Comenius University [Katedra ložiskovej geológie, Univerzita Komenského], Mlynska dolina G, Bratislava, 84215, Slovakia

E-mail: uhlik@fns.uniba.sk

Term zeoponic represents artificial soils having zeolites as a major component. Their development has emerged as one of the leading research topics in the area of using natural zeolites in the agricultural and horticultural industries for cultivation of plants. Another component frequently added to the zeoponics are apatite-rich phosphate rocks. The combination of the zeolite ion exchange capacity and slow apatite dissolution leads to optimal conditions for the slow-release fertilisation (Ming and Allen, 2001).

The possibility to use zeolite from Nižný Hrabovec for zeoponic substrates has been the main point of our interest. The volcano-sedimentary zeolite body at Nižný Hrabovec is the most important zeolite deposit in the Western Carpathians. These zeolites are clinoptilolite-rich, and they are mostly used in building industry as an admixture to cement.

The mixture of NH_4 and K-exchanged zeolites are predominately used in zeoponic substrates. Therefore five samples (pure NH_4 zeolite, mixtures of NH_4 and K zeolites in ratio 4:1, 1:1, 1:4 and pure K zeolite) were added to distilled water for 5, 30 and 60 days to determine their relationship at the releasing of exchangeable K^+ and NH_4^+. The experiment showed that the amount of released 'K and also NH_4 to a water solution depends on the total amount of K zeolite. The highest amount of NH_4 has been released by 50 and 80% content of K zeolite in the zeolite mixture.

In the next step, we prepared artificial soils following procedures published over the last 15 years (Lai and Eberl, 1986). A 1:1 mixture of NH_4- and K-exchanged Nižný Hrabovec zeolite was mixed with apatite concentrate from an unknown Russian deposit. Three zeolite-apatite mixture (1:1, 5:1, 20:1) were immersed in water and the K, NH_4, Ca, P, Na and Mg concentrations in the solution were analysed after 4 and 30 days. The phosphate concentration was increasing with increasing zeolite–apatite ratio, in agreement with previously published work. This trend indicates that the zeolites preferentially uptake Ca^{2+} from the solution, thus driving the dissolution of apatite.

Since a phosphate-rich rock similar to that used in our experiments is not available locally, we have chosen alginite as an alternative component for the zeoponic substrate. Alginite is a rock rich in algal organic matter with significant amount of clay fraction. Slovak alginite from Pincina was used. The mean contents of clay minerals on the alginite deposit are following: illite 35%, kaolinite 15% and smectite 10% (Vass et al., 1997).

Three zeolite-alginite mixtures (5:1, 1:1, 1:5) were prepared. The concentration of dissolved ions was increasing during the leaching in all mixtures. The highest ion concentration was detected in leachates from mixtures with larger zeolite proportions, regardless of whether the second component was apatite or alginite. The zeolite-alginite or zeolite-apatite mixtures were mixed with sand in three different ratios and horticulture grass was sown into these artificial soils. The grass production is higher at the alginite-based zeoponics. Similar production at the apatite-based zeoponics was achieved only for the 5:1 zeolite-apatite mixture. These differences are owing to the fact that alginite is a good soil conditioner. On the other hand the Slovak alginite has low content of N and therefore the production of grass on the pure alginite is lower than on the substrates with alginite and zeolites. Mixture of modified zeolite with alginite showed better results than commercial mixture of zeolite and fertiliser.

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GLAUCONITE OCCURRENCES IN EAST SERBIA

VASKOVIĆ, N.

Faculty of Mining and Geology, University of Belgrade [Rudarsko-geološki fakultet, Univerzitet u Beogradu], Dušina 7, Belgrade, 11000, Serbia and Montenegro

E-mail: nadavask@eunet.yu

In the East Serbian part of the Carpatho-Balkanides sediments of the Lower Cretaceous age appear in three clearly different palaeogeographic units named Carpathian (CA), Balkanian (BA) and Krajina (KA) area (Andjelković, 1975). Occurrences of glauconite are related to the Carpathian area only (Fig. 1).

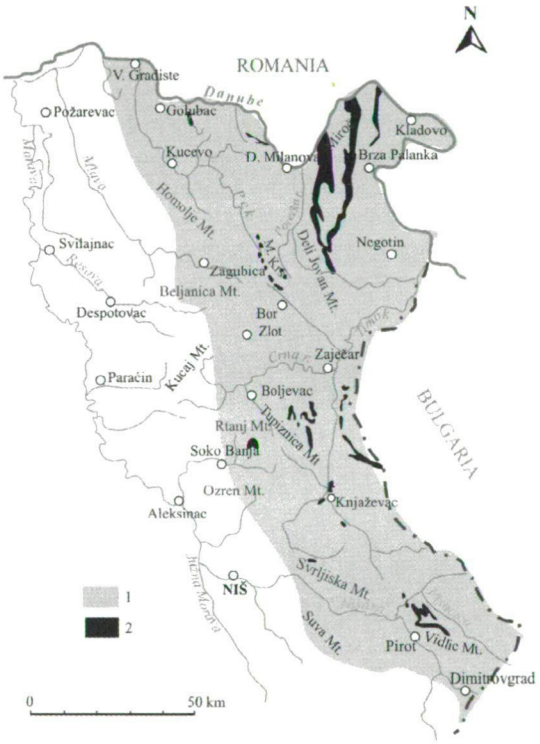

Fig. 1: Distribution of Albian and Albian-Cenomanian sediments in the East Serbian part of the Carpatho-Balkanides: 1. Carpathian area; 2. sediments of Albian and Albian-Cenomanian age with glauconite occurrences

The CA extends in the NW–SE direction and continues in Bulgaria. Differentiation of the sea bottom from the Upper Jurassic throughout the Lower Cretaceous resulted in the deposition of shallow-marine sediments. At the end of the Aptian time a large part of the CA was underwent sea-regression and later, during the Albian time, transgression. Evolved terrigeneous shallow marine sediments overlie transgressively Baremian limestones or Aptian sandstones and marls. This sediments known as Lenovac beds are rich in glauconite.

The Lower, Middle and Upper Albian are separated according to fossil fauna comprising Ammonites and shells.

The Lower Albian is composed of detrital glauconitic sandstone. The Middle Albian comprises green and red ferruginous sandstone. Sediments of the Upper Albian and Albian-Cenomanian age are the most wide-spread and overlie Middle Albian sandstones or transgressively older rocks. They are built up of green fine-grained sandstone and marly sandstone alternating with a shale rich in Ammonite species.

The Lenovac beds extend from Vlaole on the north through Krivelj, Tupiznica, Knjazevac, Trgoviski Timok, Strbce, Temska to the Mount Stara planina on the southeast.

On Mount Tupiznica Lenovac beds crop out at a few localities (Lenovac, Brzakovica, Pcela, Gornja Bela reka, Mergin grob) and comprise glauconitic sandstones and sandy marls. The coarse-grained, sometimes conglomeratic, mostly ferruginous sandstones appear as non-stratified masses of 10 to 100 m thickness and contain 45 to 60vol% glauconite. North of Mount Tupiznica, in the area between Kucevo and Bor glauconitic sandstones are slightly clayey, while east of Zajecar, on both side of river Crna reka, clayey sandstones with high amounts of glauconite (45 to 55vol%) overlie Urgonian limestone. South of Mount Tupiznica, in the area of Knjazevac and Mount Stara planina glauconite is the main constituent of detrital sandstones associated with conglomerates and marly or clayey sandstones and ferruginous limestones. On the east side of Mount Golubac (village Radenka) fossiliferous glauconitic limestones alternate with coarse-grained quartzitic sandstone and fine-grained glauconitic sandstone.

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ORIGIN OF RED CLAYS AT THE RIGHT BANK OF THE RIVER SAJÓ

VINCZE, L.,[1] KOZÁK, M.,[1] PÜSPÖKI, Z.,[1] KOVÁCS-PÁLFFY, P.,[2] BESZEDA, I.[3]

[1] Department of Mineralogy and Geology, University of Debrecen [Ásvány- és Földtani Tanszék, Debreceni Egyetem], Egyetem tér 1., Debrecen, 4010, Hungary
[2] Geological Institute of Hungary [Magyar Állami Földtani Intézet], Stefánia út 14., Budapest, 1143, Hungary
[3] Department of Solid State Physics, University of Debrecen [Szilárdtestfizika Tanszék, Debreceni Egyetem], Egyetem tér 1., Debrecen, 4010, Hungary
E-mail: vincel@freemail.hu

The department has been working on the geological mapping of the northeastern foreland of the Bükk Mountains at an observing scale of 1:10,000 since 1993. During the geological mapping several re-worked and erosional lag surfacial red clay occurrences were mapped in the Kazincbarcika–Miskolctapolca–Diósgyőr triangle. Our boreholes exposed 2–8 m thick reddish clay and palaeosol sediments near Sajóbábony.

The "red" and "reddish clays" dominantly situated on the hilltops on Miocene, Carpathian and Sarmatian various clastic deposits, subordinately on rhyolitic tuffs or on their weathered material. Re-worked by various landslides they can be found in the colluvium in a thickness up to 11 m. Red clay infillings can be found even higher than 350 m in the karst depressions of the Bükk Mountains, between 250 and 330 m in the neighbouring western side of the hills, while 190–210 m in the tectonically lowering southeastern hills. According to the latest lithostratigraphical charts they belong to the Kerecsend Red Clay Formation (Jámbor, 1998).

During the observations the surface extension of red and reddish clays we more-or-less determined and samples were taken from several outcrops and boreholes. The analysis of the grain size distribution, mineral composition (using X-ray diffraction and thermal analysis), structure (electron microscopy) and plasticity of the samples was carried out. The composition of ferrous concretions were analysed separately. The results were compared to the composition of the underlying beds, other red clays and palaeosols from North Hungary.

The red clays are reddish brown or rarely brick red, their grain size is dominantly fine sandy silt according to the scale of Atterberg. Quartz dominates in the mineral composition (51–60%) in the samples of exploring boreholes near Sajóbábony. The high amount of potassium feldspars and the 4–6% amorphous phase suggest rhyolitic tuff origin. It is supported by the dominant montmorillonite (15–20%) and illite (4–12%), while the amount of kaolinite is only 0–3%. The material is coloured by 3–4% hematite and gibbsite.

The plasticity coefficient of the samples is between 25 and 35, so they are called fat clay in soil mechanics. It correlates well with the high montmorillonite and other clay mineral content. Therefore soil creeps and fluctions, mixing of palaeosols and recent soils and the forming of thick colluvium can be frequently observed in the profiles of steep valley slopes.

During the geological mapping, profiling and drilling we found extended Sarmatian shallow marine bentonitic rhyolite tuffs contaminated with sand and silt in the hilly area, which is an important soil forming factor on superimposed lag surfaces.

Comparing to the other formations of North Hungary (Viczián, 2002; Fekete, 2002) the red clays of the area are characterised by high amount of smectite and quartz, but their kaolinite content is very low. The composition and behaviour of our samples show similarity with the so-called "nyirok" (Kozák et al., 2002) which is a kind of loam mainly formed by the weathering of tuffs, and it is less similar to the types formed by eolian materials (loess).

Hungarian red clays are dominantly aged Pliocene and Pleistocene (interglacial), however, dating is often uncertain. Age determination of cave deposits (e.g. Füköh and Kordos, 1977) give information about the age of re-working. We found mammoth tooth fragments in partly transported red clays on an uplifted hilltop near Parasznya and Pleistocene frost wedges filled with red clays and Sarmatian gravels.

To sum up, the red and reddish, partly eroded clay surface lags located to mainly Sarmatian hilltops are assumed to be the Pliocene weathering material of underlying strata which is partly eroded, partly re-worked during the strengthening tectonic and erosional dissection of Pleistocene age.

Since red clays cover extended areas they have an important economic significance. They determine the features of recent soils, the stability of slopes, the potential manner and possibilities of building up and their allochtonous occurrences even can be used as ceramic raw material.

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RECONSTRUCTION OF THE DEPOSITIONAL ENVIRONMENT OF THE MIDDLE MIOCENE PRIMATE LOCALITY, MABOKO ISLAND, KENYA

WATKINS, B. T.

Jane Herdman Labs, Department of Earth and Ocean Sciences, University of Liverpool, 4 Brownlow St., Liverpool, L69 7GP, UK
E-mail: bwatkins60@hotmail.com

Maboko Island is located in the Winam Gulf of Lake Victoria, Kenya. It has long been known for the wealth of primate fossils from the Middle Miocene. The Maboko Formation contains 20 beds that are roughly divided into a finer grained, volcaniclastic lower sequence and a relatively coarse-grained higher sequence. Benefit and McCrossin (e.g. 1997) have excavated thousands of vertebrate fossils from the lower, finer grained beds of the formation. The palaeoenvironment has been previously interpreted as the distal part of a semi-arid floodplain. However, recent findings indicate that, at least in the lower part of the sequence, the Maboko sediments display characteristics known to occur in a subaqueous environment. Sedimentologic examination of bed 3, the lowest of the fossiliferous deposits and colloquially known as greensand for its sometimes brilliant green colour, shows that a fundamental component of this bed is extremely well formed ooids. Further, subangular fragmen ts of stromatolites are found to be a minor component, and occasionally function as nuclei for the ooids. A reconstruction of the geometry of this bed indicates that it was most likely a beach ramp. The clay content in bed 3 is relatively low, but X-ray diffraction analysis indicates it is smectitic. The glycolated samples display intense 001 reflections, indicating a high-level of crystallinity. No reflections occurred between 10–17 Å. So, this bed does not contain any mixed layer illite-smectite. X-ray fluorescence spectrometry shows that the MgO content is relatively low, which appears to indicate that this bed doesn't contain Mg-smectites. However, Fe_2O_3 is reasonably high in this bed and others examined. In bed 5, the well indurated deposits generally show planar bedding, but there are instances of what appears to be relatively low angle cross-bedding. However, the apparent cross-bedding appears to be largely related to localised deformation. Further, in at least one deposit, these bedding structures have been disturbed by bioturbation. The clay content is rather low in all the well indurated deposits of bed 5, and X-ray diffraction analysis identifies them as smectites, with readings very similar to those of bed 3. The smectites from these deposits display the highest levels of Fe_2O_3. SEM investigation shows the smectites to have a „honey-combed" morphology. Analysis of the clay mineralogy of the so-called „brown lens" of bed 5, which has been the most productive of all the fossiliferous deposits, indicates that it is an illite-smectite. Glycolated samples show strong but relatively broad reflections ($d \approx 17$ Å) and moderate reflections at cca. 8.90° 2θ. Nevertheless, the relatively low clay content of bed 5, except for the „brown lens", does not appear to support the interpretation that these sediments were deposited in the distal section of a floodplain. Kent (1944) proposed that the Maboko area was the site of a vast Miocene lake, but his hypothesis was later discounted. However, in the current study, the sedimentology appears to support Kent's hypothesis.

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NANOMATERIALS BASED ON INTERCALATED CLAY MINERALS

WEISS, Z.,[1] KŘÍSTROVÁ, M.,[1] VALÁŠKOVÁ, M.,[1] SEIDLEROVÁ, J.,[1] ŠUSTAI, O.,[1] ČAPKOVÁ, P.[2]

[1] Institute of Materials Chemistry, Technical University of Ostrava [Vysokoškolský ústav chemie materiálů Technická univerzita Ostrava], tř. 17. listopadu 15, Ostrava–Poruba, 708 33, Czech Republic

[2] Department of Chemical Physics and Optics, Charles University [Katedra chemické fyziky a optiky , Univerzita Karlova], Ke Karlovu 3, Praha, 121 16, Czech Republic

E-mail: zdenek.weiss@vsb.cz

Intercalates of montmorillonite with octadecylamine were synthesised using low-temperature melting procedure to obtain precursors for polymer nanocomposites. Results of the interlayer structure analysis show that observed values of interlayer spacing depends on the concentration of octadecylamine molecules in the interlayer. The spacing equal to 33 Å (monolayer arrangement) and 53 Å (bilayer arrangement) were observed for the following ratios of montmorillonite–octadecylamine = 100:75 and 100:150, respectively. The intercalation reaction is based on the ion–dipol interaction and the both interlayer species (Na^+ cations and polar molecules of octadecylamine) participate in the host-guest charge transfer. The values of calculated exfoliation energy confirmed the generally accepted opinion that the exfoliation is more easy for the bilayer arrangement of the guests and that the increase of the octadecylamine concentration decreases the exfoliation energy. Resulting montmorillonite–octadecylamine intercalate with the bilayer arrangement in the interlayer is a suitable precursor with low exfoliation energy for clay–polymer nanocomposite technology.

Nanoparticles suitable for clay–polymer nanocomposite were also prepared by exfoliation and disintegration of vermiculite powder (< 5 μm) using 30% hydrogen peroxide treatment. Significant reduction of the peak intensity of the 002 reflection was observed (there is only 14% of the intensity of non-treated sample) after treatment of the sample with hydrogen peroxide (30 minutes at 50°C). Reduction of the peak intensity of basal reflections is caused by disintegration of vermiculite particles and the hydrogen peroxide treatment is decisive for this process. We suggest at least two possibilities for fixation of peroxide in the Mg-vermiculite structure: a) intercalation of peroxide molecules into the interlayer (addition of peroxide molecules to water molecules), and b) substitution of H_2O_2 molecules for H_2O molecules. Combined thermal (at 50°C) and peroxide treatments cause the significant degree of Mg-vermiculite exfoliation and disintegration.

Crystallisation of nanoparticles of CdS in the interlayer "space reactor" of montmorillonite was performed and changes in the XRD and IR patterns were observed. Such intercalated system is related to the recent discovery that the photophysical properties of semi-conductors change with particle size. A shift of spectral absorption threshold was observed when CdS nanoparticles powder and montmorillonite intercalated with CdS nanoparticles were compared.

THE CRYSTAL CHEMICAL EVOLUTION OF GLAUCONITES

WEISZBURG, T. G., TÓTH, E.

Department of Mineralogy, Eötvös Loránd University [Eötvös Loránd Tudományegyetem Ásványtani Tanszék], Pázmány Péter sétány 1/C, H-1117, Budapest, Hungary
E-mail: weiszburg@ludens.elte.hu

This is the first comprehensive report on the study of three glauconite populations from the Upper Oligocene sandstones of the Eger Formation, North Hungary. Two samples originate from Nyárjas summit (Novaj, samples #Ny1 and #Ny3) and the third sample comes from the type section of the Eger Formation (Eger, Wind brick yard, sample #EWT).

The samples have been treated with dilute (5%) acetic acid to remove carbonates, the detrital and glauconitic grains have been separated upon grain size, magnetic susceptibility (0.5, 0.6, 0.7 and 0.8 A) and density (2.33–2.83 g/cm^3 density range, step size 0.05 g/cm^3). The final separation step was hand-picking under the stereomicroscope. The glauconite populations were characterised by powder XRD, FTIR, main (WDX, EDX, ICP-OES) and trace (LA-ICP-MS) element chemistry.

Although originating from the same formation, the three samples exhibited significantly different characteristics. Sample #Ny1 represents a complete evolution series from the lowest to the highest densities, while #EWT is a highly evolved population of mainly high density grains and #Ny3 is a less evolved population with the dominance of low density fractions.

The substrates of the glauconitic grains differ, too: the substrate in #EWT is volcanic debris only, while in the other two samples both volcanic debris and biogenic grain (foraminifera tests, faecal pellets, echinoderm fragments and snails) substrates are present. Glauconites of #EWT are allochthonous while those of the two other samples are autochthonous.

The smectite-mica structural evolution (see e.g. Wiewióra and Lacka, 1985) is detectable on the powder XRD patterns of all the three samples; however, each population is characterised by a specific and constant d_{060} value (1.515, 1.517 and 1.521 Å for #EWT, #Ny1 and #Ny3, respectively).

As confirmed by main element chemistry, the populations basically preserve their tetrahedral trivalent cation proportion. As expected, the d_{060} value relates to the tetrahedral cation proportion: the higher the trivalent cation substitution, the higher is the d_{060} (0.20–0.25 p.f.u. for #EWT, 0.40–0.45 p.f.u. for #Ny1 and 0.50–0.60 p.f.u. for #Ny3, respectively; formula unit is always calculated for 11 O atoms). Concerning octahedral occupancy, samples #Ny3 and #Ny1 decrease from 2.2 to 2.0 p.f.u., while #EWT decreases from 2.1 to 2.0 p.f.u. The different evolutionary stage is reflected in the different interlayer charge ranges: 0.45–0.90 p.f.u. for #Ny1, 0.50–0.85 p.f.u. for #Ny3 and 0.50–0.90 p.f.u. for #EWT. The reworked and diagenetically altered nature of #EWT is reflected in the main chemistry: data are a little scattered and increasing density fractions are not strictly following the expected chemical evolution trend.

The REE content of glauconite is dependent on the substrate type but also on diagenetic processes: #Ny1 and #Ny3 reveal decreasing REE content with increasing evolutionary stage while #EWT has an increasing REE content due to the postgenetic precipitation of REE-Ca phosphates (with the dominance of Ce). Within a given density fraction, usually faecal pellets have the highest, echinoderm test fragments the lowest REE-content (analytical error due to high porosity cannot be entirely excluded), while other biogenic grains and rock fragments have overlapping values within the two extremes. Glauconites exhibit negative Ce and Eu anomaly (normalised to PAAS), except for #EWT, which has positive Ce anomaly due to the above mentioned phosphate precipitation.

Based on the clear, from diagenesis undisturbed example of #Ny1, both the structural and crystal chemical evolution steps of glauconitisation were recorded. The gradual incorporation of K, Fe^{2+} and Fe^{3+} into the structure parallel to the release of Al (for a comprehensive overview see Odin and Fullagar, 1988) have been confirmed by bulk chemistry. Due to the chemically stable tetrahedral sheet, the increase in the interlayer charge is compensated by the decrease of the cationic charge of the octahedral sheet. Three substitutions take place in the octahedral sheet: (1) Al => Fe^{3+}, (2) Al => Fe^{2+}, (3) Al => □ (vacancy). The second substitution process decreases only the octahedral cation charge, while the third one decreases both the octahedral occupancy and the octahedral cation charge. The latter two substitutions are equally significant in compensating the increase in the interlayer charge.

This work has been supported by the SYS-Resource Programme of the European Community and the Natural History Museum (London) and by the Hungarian Science Foundation (OTKA) grant T25873.

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CRYSTAL CHEMISTRY OF TALC: XRD AND SPECTROSCOPIC STUDIES

WIEWIÓRA, A.,[1] PETIT, S.,[2] MARTIN, F.,[3] PROST, R.[4]

[1] Institute of Geological Sciences PAS [Instytut Nauk Geologycznyh PAN], Twarda 51–55, Warszawa, 00 818, Poland
[2] HydrASA Laboratoire, Université de Poitiers, 40 av. du Recteur Pineau, Poitiers, 86022, France
[3] HydrASA Laboratoire d'Analyse Structurale et Hydrothermalism, Université de Limoges, 123 av. Albert Thomas, Limoges, 87060, France
[4] Laboratoire de Science du Sol INRA, r. de Saint-Cyr, Versailles, 78026, France
E-mail: wiewiora@twarda.pan.pl

In the monolithic (non powdered) samples of talc Wiewióra (1997) determined superstructure, characterised by $d_{(001)}$ = 18.7 Å with integral series of $d_{(001)}/l$ until l = 18, while X-ray tracings of powdered aggregates showed only all the talc common peaks. The strongest reflection for powder is 001, while it is 003 (006 of superstructure) for quasi single crystal sample. From intensities of the basal reflections, divided by Lorentz-polarisation factor for single crystal, a one-dimensional Fourier analysis was performed. It revealed increase in the electron density, right in the middle in the talc interlayer space (Fig. 1). This additional electron density band correlates rightly with a very strong vibration at 101 cm^{-1} in the far infrared, for the first time obtained on monolithic sample, while this band is hardly visible in this position in the spectra from powdered sample. This band clearly indicates some Mg in the interlayer space of talc.

There is no direct proof for the occupation of structural positions in talc by Ca, Na, K but positive correlation of Na with tetrahedral Al (R^2 = 0.71) may indicate that some Na may enter also the interlayer positions to enable charge balance due to tetrahedral substitution of Si by lower-valency cation, namely Al and/or Fe^{3+}.

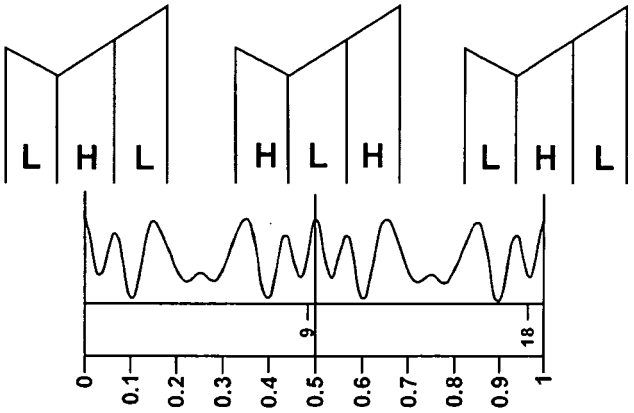

Fig. 1: One-dimensional [001] electron density distribution for two layer structure of talc.

Medium infrared Fourier spectroscopy revealed, in some samples of talc, νMg_3OH (band present in all spectra), but also νMg_2FeOH, $\nu MgFe_2OH$, νFe_3OH and for the first time νMg_2AlOH band. In the same samples $2\nu Mg_3OH$, $2\nu Mg_2FeOH$, $2\nu MgFe_2OH$, $2\nu Fe_3OH$ and $2\nu Mg_2AlOH$ vibrations were for the first time recorded in the near infrared spectral region. The spectra proved presence of Fe and Al substituting Mg in the octahedral positions of talc and enabled their quantification (Petit et al., 2004). Mössbauer technique, as applied to study four samples, demonstrated that 62–68% of iron is as Fe^{2+} located in octahedral positions. Fe^{3+} is located in the octahedral and tetrahedral positions. The determined distributions of Fe^{2+} between M(1), M(2) and M(3) octahedral positions appear to depend on temperature in which experiment was performed. At 80 K the two different octahedral occupancies of Fe were differentiated, but three occupation positions at 4 K.

These XRD and spectroscopic data may mean that our understanding of talc structure as polytype $1A_A$–II ($|^e_5{\cdot}^e_1|$), belonging to C–1 space group (more or less disordered) may be not adequate with real structure of some individual samples. In several samples of talc, originated by transformation of e.g. micas or chlorites, superstructure is quite evident. In the light of one-dimensional electron density by Fourier transforms analysis, the structure may be explained as two layer arrangement with the basal spacing $d_{(00l)}$ = 18.7 Å. In each pair of layers, having different electron densities of octahedral sheets (possibly tetrahedral, also), the even (e) orientation of octahedral sheet, intra-layer displacement along <5> vector and interlayer displacement of tetrahedral sheets belonging to adjacent layers along <1>, produce resultant layer displacement <0>. Such a structure (Fig. 1) gives superstructure reflections in XRD pattern.

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CRYSTAL CHEMISTRY OF TALC: CHEMICAL STUDY

WIEWIÓRA, A., WILAMOWSKI, A.
Institute of Geological Sciences PAS [Instytut Nauk Geologycznyh PAN], Twarda 51–55, Warszawa, 00 818, Poland
E-mail: wiewiora@twarda.pan.pl

The present work was based both on published data on talcs and on our own talc analyses. The total number of chemical analyses of talcs exceeded 120. Chemical compositions of talc show various elements, such as Fe, Al, Cr, Ni, Mn, alkalies and fluorine. Several analyses of talcs from Egypt (El-Sharkawy, 2000) show the rectilinear negative correlation of Si and Fe^{3+} suggesting simultaneous substitution of Fe^{3+} both in tetrahedra and in octahedra according to the mechanism $MgSi \leftrightarrow Fe^{3+}Fe^{3+}$. This was verified in talcs deficient in Si and rich in Fe. Essentially better calculated formulas and agreement of the layer charge with the theoretical value 22 were achieved after recalculation of Fe oxidation state according to the above mentioned scheme (Fig. 1). The highest Fe^{3+} contents demonstrate talcs from low-temperature crystallisation environments. The likely explanation is interaction with pore fluids.

Chemical compositions of octahedral sheet, plotted in the ternary diagram Mg-Al-Fe+Mn+Ni+Zn, demonstrate a quite regular grouping of projection points into three fields: I) near-stoichiometric talcs around 100% Mg; II) talcs with elevated Fe+Mn+Ni+Zn contents and III) Mg-Al talcs. Samples representing all genetic types gather in the first field, in the second dominate talcs from high pressure and ultramafic environments, and in the third dolomite related talcs (Fig. 2).

The positive correlation of tetrahedral Al and Na (R^2 = 0.71) suggests the substitution mechanism involving the tetrahedral sheet and interlayer space: $NaAl \leftrightarrow Si$ (Fig. 3). Much weaker correlation shows octahedral Al (R^2 = 0.50). Sodium content shows positive correlation both with temperature and pressure of talc crystallisation. It is likely that high PT conditions favour incorporating Na into the talc structure.

No correlation was observed between chemical composition and structural varieties of talc, expressed as the presence or absence of structural and/or superstructural diffractions in powder diffraction patterns.

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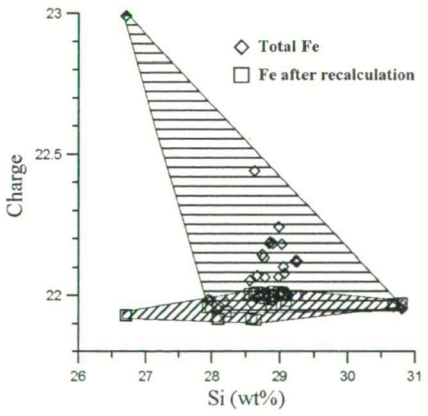

Fig. 1

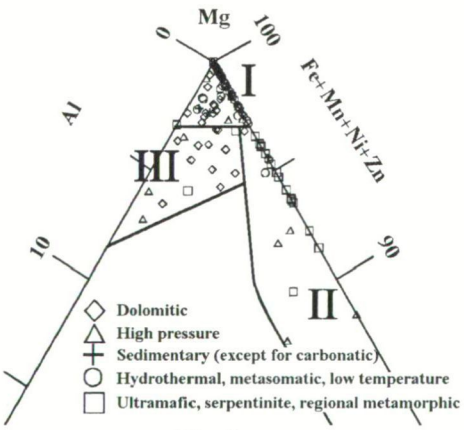

Fig. 2

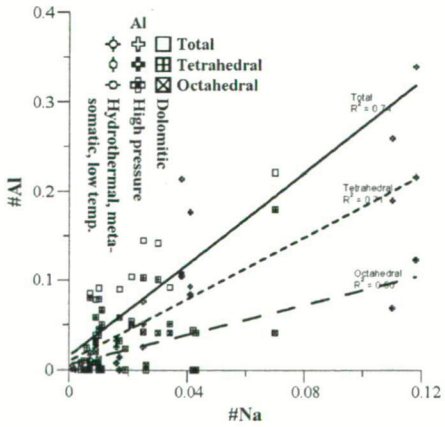

Fig. 3

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CLAY MINERALOGY OF THE P/Tr BOUNDARY SECTION OF BÁLVÁNY HILL, BÜKK MOUNTAINS, HUNGARY

ZAJZON, N.,[1] WEISZBURG, T. G.[2]

[1] Department of Mineralogy and Petrology, University of Miskolc [Miskolci Egyetem Ásvány- és Kőzettani Tanszék], Egyetemváros, Miskolc, 3515, Hungary

[2] Department of Mineralogy, Eötvös Loránd University [Eötvös Loránd Tudományegyetem Ásványtani Tanszék], Pázmány Péter sétány 1/c., Budapest, 1117, Hungary

E-mail: nzajzon@hotmail.com

In the frame of a multidisciplinary research project we are studying the Permian/Triassic (P/Tr) boundary, for a better understanding of the dramatic and abrupt ecological change in this period. At the P/Tr boundary about 95% of the marine species became extinct (Sepkoski, 1996). The current presentation is a report of some of the clay mineralogical data in a Hungarian geological section crossing this boundary.

Our section is located close to the top of the Bálvány Hill in the Bükk Mountains (about 120 km northeast of Budapest). This is a composite section, exposed in two outcrops within a distance of a few hundred m from each other. The outcrop containing the lower part of the section is situated on the northern slope of the hill and is called "Bálvány North". The upper part of the section is cropping out at the eastern side of the hill and is referred to as "Bálvány East". The section contains the top of the black, thick bedded Nagyvisnyó Limestone Formation and the lower part of the Gerennavár Limestone Formation. The Gerennavár Limestone Formation starts with the fine-grained siliciclastic "Basal Bedset" followed by the thin bedded "Transitional Bedset" (Hips and Pelikán, 2002).

The uppermost part of the Nagyvisnyó Limestone turns to a marl, the HCl insoluble part of it increases from 2 to 40%. Going further upward follows the very homogeneous Basal Bedset of an average carbonate content of 26% only, except for a 2 cm thick limestone and a 3 cm thick sandstone layer (Zajzon, 2003). The thin bedded Transitional Bedset consists of limestone interlayered by marl and clay horizons.

In the section the HCl insoluble residue consists mainly of clay fraction minerals. The larger size terrigeneous grains are rare, except for the above mentioned 3 cm thick sandstone layer in the Basal Bedset. This layer is a fine-grained sandstone cemented by carbonate. It contains much (two magnitudes) higher amount of terrigeneous grains than any other beds from the section. The heavy mineral population is very mature. Zircon represents most of the grains. The rest are tourmaline and rutile, some actinolite is also present (Zajzon, 2003).

For clay mineral studies the collected samples have been crushed and decarbonated by 5 vol% CH_3COOH. After washing to neutral pH, the < 10 μm fraction has been separated by sedimentation, applying Stokes' law. The clay fractions were measured by X-ray diffractometry on non-oriented, oriented untreated and oriented ethylene glycol treated samples.

The clay minerals of the section are kaolinite (7.1 Å), a 10 Å phase (muscovite, illite) and smectite (14.2–14.4 Å). Usually kaolinite is dominant. For ethylene glycol treatment the 14.2–14.4 Å reflection of smectite shifts to 16.5 Å. This clay mineral pattern does not change from the Permian to the Triassic in the section: there is no indication of any tuff layer or other volcanic activity, just the relative carbonate amount changes from layer to layer.

The lack of the change in the clay mineral spectrum is similar to another P/Tr transition zone (Gárdony–1 borehole) in the Transdanubian Unit, where the dominating clay mineral is illite (Zajzon, 2003).

Acknowledgements

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CLAY MINERALS IN LAND MOVEMENTS AT HOLLÓHÁZA, TOKAJ MOUNTAINS

ZELENKA, T.,[1] KOVÁCS-PÁLFFY, P.,[2] TRAUBERT, N.[3]

[1] Hungarian Geological Survey [Magyar Geológiai Szolgálat], Stefánia út 14., Budapest, 1143, Hungary
[2] Geological Institute of Hungary [Magyar Állami Földtani Intézet], Stefánia út 14., Budapest, 1143, Hungary
[3] Keviterv Plusz Ltd., Katalin u. 1., Miskolc, 3527, Hungary

Hollóháza is in the northeastern part of Hungary, in the Tokaj Mountains region neighbouring Slovakia. This is a potential area for land movements which derives from the characteristic geological structure of the mountains. There were several unfortunate examples in the recent past for showing the real nature of this phenomenon.

The region of the Tokaj Mountains used to be the part of a former volcanic archipelago, constantly sinking in the Middle-Upper Miocene between fault lines stretching to Hernád and Rongyva streams (NE–SW, NW–SE). Volcanism was calc-alkalic in nature which, in two cycles, resulted in rhyolitic-rhyolitic tuff an then andesitic-dacitic and basaltic-andesitic lava and debris during the Badenian and Sarmatian stages.

Hollóháza is surrounded by the ring-shaped wrecks of the former trenches of a Miocene volcanic caldera, 4–6 kms in diameter. These peaks form the watershed rising over the village by 250–300 m at 500–600 m. The inner area is about 20 km^2, into which approx. 12 million m^3 water quantity filters and runs down to the catchment area of Török stream every year on average out of 600–650 mm rainfall. The rainfall flows towards the village from all directions down the steep slopes, partly as surface water flows and water from the aquifers, partly as fissure water.

The village settled down in the natural cirque of the former caldera. Here rhyolite tuff and clayey sea sediments of various thickness (10–20 m) and volumes (< 20 km^2) are settled on the base andesite. On their border, wells from aquifers are sprung on the valley bottom. The cirque-like depression is divided into two from northwest to southeast by a huge tectonic valley showing lateral movement (Török stream valley). In the southeast it breaks through the trenches of the former caldera like a gorge. From east and west towards the tectonic valley clay and rhyolite tuff layers lean with 10–25%.

The rhyolite tuff with different grain sizes originally fallen into water and alternating with Sarmatian sea clays has been strongly become clayey but the covering humus has a high clay mineral content, too. These rocks swell due to getting in contact with water and slides happen to occur on their surfaces. Andesitic rocks in the basement also became clay mineralised, strongly contributing to the occurrence of slumps.

These geological formation cause different land movements in size due to the high swelling clay mineral content. 11 potential hazardous areas can be delineated in Hollóháza, from which the most dangerous are the southern side of Nagy Hrabó Mount (1.5 million m^3 moved mass), surroundings of the Roman Catholic church (0.3 million m^3) and surroundings of Attila József residential area (2.5 million m^3).

Different slides can be slumps, earth sinks and glides morphologically causing serious damages to buildings, road and public utility networks. Inside the village, at the upper part of Rákóczi Road and near the Porcelain Factory land movements are not present because these are settled on massive lava rocks. Other parts of the village are settled on formations consisiting of strongly clay-minerals-bearing Sarmatian clay alternating with rhyolite tuff which is slide hazardous to a greater extent due to the swelling ability of clay minerals and plays an important role in the damaging changes of the surface.

Table 1: The swelling clay mineral content of rocks in %

Formation	Montmorillonite	Illite-montmorillonite
Humus	29 (20–43)	4 (0–5)
Sea sandy clay	24 (12–50)	4 (0–6)
Rhyolite tuff	52 (34–81)	1 (0–6)
Andesite	74 (58–91)	–

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TEMPERATURE AND PRESSURE EFFECTS ON SMECTITE-ILLITE DIAGENESIS REVEALED BY WELL LOG MEASUREMENTS

ZUGRĂVESCU, D., POLONIC, G., NEGOIȚĂ, V.

Institute of Geodynamics RAS [Institutul de Geodinamică ASR], str. Jean-Louis Calderon 19–21, București, 70201, Romania
E-mail: dorezugr@geodin.ro

During the last six years many research programs of the Institute of Geodynamics were directed to topics related to the various geodynamic processes taking place in the Vrancea region, a well defined European seismo-active area; and a geodynamic polygon representing an area of 30,000 km^2, delimited by the 26° and 27°30' meridians and the 44°30' and 46° parallels, incorporating the Vrancea region, was set up for experimental works.

At the same time, the geodynamic polygon area attracted our attention due to the huge volume of borehole geophysical measurements coming from more than 3000 wells, drilled in the depth interval 0–7025 m, for exploration and exploitation of hydrocarbon resources. The thick Miocene and Pliocene detritic sedimentary sequence penetrated by these boreholes was rapidly and deeply buried, giving rise, in sealed pores, to very high overpressures in the fluids of rocks.

According to our studies, the most important mechanism related to this overpressure generation are the aquathermal pressuring effect and the smectite-illite diagenesis.

The aquathermal pressuring phenomenon has been much discussed in the literature and a previous work carried out at our institute demonstrated the prevalent role of this overpressure mechanism in our area of study, where fluid pressure gradients reach 22 MPa/km.

As far as clay diagenesis is concerned, the chemical reaction involving smectite-illite transformation by K fixation, which releases a significant amount of bound water from clay platelets into the rock pore space, may also be considered, to a certain extent, a cause of the high overpressures recorded.

Such a process was reported by many authors as being kinetic in nature and controlled by the temperature and time history of sediment burial. Most of them indicated that such a chemical reaction is mainly a function of temperature and typically begins between 60°C and 80°C.

For instance in the Gulf Coast shales, illite-smectite is 20–80% before the diagenesis starts, progresses to 80–20% mix at about 140°C, finishing with a complete illitisation above the temperature of 250°C.

In the above mentioned rocks the customary techniques used for smectite-illite investigation were based on X-ray laboratory analyses accomplished on a preselected number of cores, samples drawn from boreholes.

Nevertheless, without any extra cost, the same objectives can be approached using the continuous measurements of well logs recorded in each borehole. It has been proved that such a technique was very suitable in a region such as our geodynamic polygon, where the number of recovered cores from geological formations is scanty.

The Miocene–Pliocene sedimentary pile is constituted of sand-shale series in which montmorillonite is the most frequent argillaceous component.

Open hole investigations comprise electric, radioactive and sonic logs. Wildcat and discovery drillings include yet more measurements, such as the lithodensity log and natural gamma ray spectrometry.

Such exquisite measurement, performed by Schlumberger equipments, supplied basic data to appreciate both the Compton scattering low-energy gamma ray interactions and the photoelectric effect arising occurring during the subsequent absorption process of gamma rays. Natural gamma ray spectrometry in its turn supplies continuous measurements of the following three radioactive isotopes: ^{40}K, ^{238}U and ^{232}Th. Because the different clay minerals have characteristic concentrations of K, U and Th, the continuous logs recorded in the boreholes have been used to identify the types of clay minerals.

Field data coming entirely from the geodynamic polygon have been processed according to Schlumberger instructions. Eight boreholes were selected to completely cover the depth interval 600–6000 m, allowing the precise monitoring of clay mineral conversion from montmorillonite to mixed layer and afterwards to illite.

All graphical presentations and interpretation are displayed on the poster. Conclusions can be summarised in the following points: a) the use of well logging measurements provide the most complete information for smecite-illite diagenesis; b) the above mentioned clay mineral conversion is kinetic in nature and seems to start almost immediately after sediment deposition; c) the higher the geothermal gradient during sediment burial, the faster is the conversion rate; d) the high lithostatic pressure gradients lead to an obvious slowing down of the illitisation process.

AUTHOR INDEX

Készült a mondAt Kft. nyomdájában
Felelős vezető: Nagy László
Tel.: 06 30 944-9332

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The abstract is required to be brief (max. 250 words), and has to highlight the aims and the results of the article. The abstracts of notes are alike (but max. 120 words). As far as possible, citations have to be avoided. In the near future the abstracts are going to be distributed in digital form as well. The abstract has to be followed by 4 to 10 keywords.

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The format of the manuscripts is required to be: double-spacing (same for the abstract), text only on one side of the page, size 12 Times New Roman fonts. Margin width is 2.5 cm, except the left margin, which has to be 3.5 cm wide. Underlines and highlights ought not be used. Accents of Romanian, Slovakian, Czech, Croatian etc. characters must be marked on the manuscript clearly.

When compiling the paper an Introduction - Geological setting - Materials and Methods - Results - Conclusions structure is suggested.

The form of citations is: the author's surname followed by the date of publication e.g. (Szederkényi 1996). In case of two authors: (Rosso, Bodnar 1995). If there are more than two authors, after the first name the co-authors must be denoted as "et al.", e.g. (Roser et al. 1980).

REFERENCES

The reference list can only consist of published papers, M.Sc., Ph.D. and D.Sc. theses, and papers in press.

Only works cited previously in the text can be put in the reference list. Examples:

Szederkényi, T. (1996): Metamorphic formations and their correlation in the Hungarian part of Tisia Megaunit (Tisia Megaunit Terrane). Acta Mineralogica-Petrographica, **37**, 143–160.

Rosso, K. M., Bodnar, R. J. (1995): Microthermometric and Raman spectroscopic detection limits of CO_2 in fluid inclusions and the Raman spectroscopic characterization of CO_2. Geochimica et Cosmochimica Acta, **59**, 3961–3975.

Roser, B. P., Childs, C. W., Glasby, G. P. (1980): Manganese in New Zealand. In Varentsov, I. M., Grasselly, Gy. (eds.): Geology and Geochemistry of Manganese, Vol. II., 199–211. Akadémiai Kiadó, Budapest.

Nesse, W. D. (2000): Introduction to Mineralogy. Oxford University Press. 442 pp.

Pál-Molnár, E. (1998): Geology and petrology of the Ditró Syenite Massif with special respect to formation of hornblendites and diorites. Ph. D. thesis, University of Szeged, Szeged, Hungary. 219 pp.

The full titles of journals ought to be given. In case more works of the same author are published in the same year, then these has to be differentiated by using a, b, etc. after the date.

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Dr. Pál-Molnár Elemér
E-mail: plam@geo.u-szeged.hu
Phone: +36-62-644-683, Fax: +36-62-426-479
Department of Mineralogy, Geochemistry and Petrology
University of Szeged
P.O. Box 651
H-6701 Szeged, Hungary

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